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Schimmel & Co.

SEMI-ANNUAL REPORT

OF

SCHIMMEL & Co.

(FRITZSCHE BROTHERS)

MILTITZ

NEAR LEIPZIG

LONDON • NEW YORK.

OCTOBER/NOVEMBER 1906.

Contents.

List of abbreviations.

d = specific gravity.

d_{20° = specific gravity at 20°, compared with water at 15°.

$d\frac{20^\circ}{4^\circ}$ = specific gravity at 20°, compared with water at 4°.

α_{D20° = optical rotation at 20°, in a 100 mm. tube.

$[\alpha]_D$ = specific rotation.

n_{D20° = index of refraction at 20°.

Sol. p. = solidifying point.

M. p. = melting point.

B. p. = boiling point.

n = normal.

Acid no. = acid number; ester no. = ester number; sap. no. = saponification number.

g. = gram; cc. = cubic centimeter; mm. = millimeter.

Temperatures are uniformly given in degrees Centigrade.

The strength of alcohol, if not otherwise indicated, is given in per cent. by volume.

Miltitz near Leipzig, October/November 1906.

The period which has elapsed since the date of our last Report is one of which, on the whole, a favourable description can be given, for we are able to look back upon months of brisk activity, during which the output has been increasing in a healthy proportion. Our own industry of the essential oils has also, generally speaking, participated in the favourable conditions, and it is satisfactory to note that the new German Tariff, of which the coming into force was looked upon at the beginning of the year with a reasonable feeling of uncertainty, has not had an injurious effect on our branch of industry, in spite of the fact that the resale of foreign products plays such an important part in this branch. The clouds of Algeciras which at the time when our last Report was published, still cast a dark shadow on the political horizon towards the West, have meanwhile disappeared, and the meeting of the monarchs at Friedrichshof, which has produced an entirely favourable impression in the international press, makes it appear as if a state of unrest in the politics of the Great Powers of Europe were out of the question for the near future. Although it cannot be denied that the still thoroughly unsettled state of affairs in Russia may, under certain conditions, exert an injurious influence on our industrial activity, it may be doubted whether, in case it should take a fatal turn, it would cause a serious convulsion of the economic conditions of Germany.

The sale of our products in France has again increased considerably during the last few months, since the chauvinistic spirit has calmed down, and the mutual neighbourly confidence has been re-established by the settlement of the Moroccan question. Our London branch has also been very fully employed, and we can state with satisfaction that our relations with the United Kingdom and its Colonies show a steady and healthy development.

Our branch in Austria, at Bodenbach o. E., also shows important progress. The commercial situation in Austria-Hungary is not unfavourable for those industries which consume our products, although naturally the political dissensions within that monarchy also cast their shadows on the future. It is to be hoped that an adjustment of the differences between Austria and Hungary may yet be brought about.

In spite of the confusion in Russia of which the end is not nearly in sight, trade with this desirable market for our articles has increased still further; and although it is obviously necessary to exercise caution in the commercial intercourse with a country which is in such a deplorable critical state, we have yet found by experience that there is no lack of firms well supported by capital and able to pass through the present crisis as if it were a disease of a temporary character.

The trade with Italy, Switzerland, and Holland does not give rise to any special remarks.

The commercial intercourse with Spain unfortunately still suffers from the effects of the alcohol-law which has been in force since October 1st, 1904, and which in the main secures to a few important manufacturers alone the monopoly of the brandy and liqueur production, whilst it has crippled small industries. The alcohol-reform bill promoted by the parties affected has unfortunately not yet become realised, as owing to the continuous change of ministries the Government has not sufficient leisure to take in hand such a reform with any chance of success. During the last twelve months, no fewer than four different cabinets took up the reins, and each party which came into power again appointed fresh commissions for the purpose of making a thorough study of the industries affected. In every instance months passed by without any tangible results, and in the meantime, the existing Government had again made room for a new one. The present Spanish parliament has now other points on the order-of-the-day; when these have been dealt with, the alcohol-reform bill may perhaps come up for discussion in the course of January 1907 — assuming, of course, that the existing Government has not by that time been supplanted.

The trade with the Balkan States and also with the Orient proper was very brisk. It is satisfactory to note that also in those countries the due appreciation of quality has made considerable progress, and that it is gradually recognised that certain firms are in the habit of looking upon those districts as welcome markets for inferior and "cheap" products. The relations with Roumania (which country has this year been favoured with a rich harvest) are constantly extending, whilst the sale of our products in Servia has suffered much from the tariff-war between that country and Austria-Hungary, — a dispute in the satisfactory settlement of which Germany, as a "most-favoured" nation, naturally is greatly interested.

The trade with the United States of America continued brisk, and all symptoms point to a continuation of the favourable commercial situation in this important market. The regrettable catastrophe of the earthquake of San Francisco has had no real influence on business

in the Far West, and the favourable effect of the record harvest of 1906 is making itself felt in the increased inclination of the interior to buy. The import of essential oils from Germany during the last three fiscal years was as follows: —

	1902/03	1903/04	1904/05
duty-free . .	\$ 892122,—	\$ 549222,—	\$ 862946,—
dutiable . .	„ 404442,—	„ 506633,—	„ 551007,—

The National Pure Food Law (an Act for preventing the manufacture, sale, transportation of adulterated or misbranded or poisonous or deleterious foods, drugs, medicines, and liquors, and for regulating traffic therein, and for other purposes) will become a statute on January 1st, 1907.

This kind of legislation is surely in the right direction and it is to be hoped that said law will be rigidly enforced.

The standard for raw materials entering into food-products, drugs and medicines to be imported in the U. S. will surely be raised to a pre-eminent degree and it is to be expected that the employment of pure essential oils and related articles which we have advocated in these Reports for so many years will now become predominant.

The Rules and Regulations for carrying out the provisions of this new Law have just been published.

In the Argentine Republic the sale of our products has undergone a further favourable development, whilst Chile, which was in a period of undoubted progress, has suffered through the earthquake a blow of which the consequences cannot as yet be fully estimated. With regard to the importation of German products of the chemical industry, drugs and pharmaceutical specialities in Brazil, a report from the Imperial Consulate General at Rio de Janeiro shows that Germany, in respect of the average value of her sales in the years 1902 to 1904, occupies the first place. Although the development of the home industry has been assisted by high duties, it is up to the present still very insignificant, with the exception of the soap- and salt-industries, and for this reason the importation of chemical products may possibly increase further. If the competition against England, America and France is carried on seriously, the imports from Germany are capable of a considerable expansion. According to our own statistical notes, the export of our specialties to Brazil is experiencing a slow but continued growth.

The export of our products to Japan during the past half-year was exceptionally brisk, and the increase in the import duties contemplated for October 1st, 1906, which in the case of our articles amounts from 10 to 20%, led to a demand such as we had not experienced before in our intercourse with this important market.

The effect of this new tax on the consumption cannot yet at present be estimated; during the last few weeks the inclination to buy has visibly fallen off, and it would appear that for the present buyers will take up an expectant attitude. It is to be hoped that the excellent results of this year's rice-harvest will exert a beneficial influence on the trade.

According to the official statistical tables, the value of essential oils imported in Japan during the first six months was: —

1906	1905	1904
147 523 yen	125 561 yen	67 997 yen

This shows sufficiently the large increase in business during the last two years.

An article in the "Oil and Colourman's Journal", published in London, is interesting and characteristic of the development of the soap-industry which consumes our products. This article states that the most important soap-works of Japan are situated in the neighbourhood of Osaka, and that the value of their output fluctuates between 30 000 and 300 000 yen per annum. The total production amounts to about 750 000 yen. Of this, about 70 % are said to be consumed in Japan itself, whilst the balance is exported to China, Korea, the Philippines, and the West Indies. In spite of the medium quality of Japanese soap, the exports via Osaka and Kobe increase from year to year:

		Toilet Soap		Common Soap
1902	about	168 000 yen	about	24 000 yen
1903	„	190 000 „	„	31 000 „
1904	„	311 000 „	„	43 000 „

Although the quantity of the soap imported in Japan during the same years has not fallen off in a marked degree, its value has during that period decreased from 150 000 yen to about 105 000 yen, i. e. by nearly one third.

On January 1st, 1907, a new edition of the Japanese Pharmacopœia comes into force, of which a translation has unfortunately not yet come to hand, and the critical discussion of which we must therefore postpone until later. The importation of remedies corresponding to the P. J. II will be allowed until the end of next year, provided every package carries a stamp worded in accordance with regulations specially issued.

With regard to the price-fluctuations in our branch, and the progress in the interesting scientific domain of the essential oils and kindred preparations in the course of the last half-year, the following pages give information which we trust will be of interest in one way or another to everyone of our readers, although some of the commercial

data will already be found distanced by the events whilst these pages were in the press.

Professor Dr. R. Kobert, Director of the Institute of Pharmacology and Physiological Chemistry at the University of Rostock, has again been kind enough to allow us to publish a work composed in his laboratory by Mr. Karl Kobert, "Systematic experiments on the antiseptic action of essential oils and their constituents", for which we desire to express in this place once more our sincere thanks.

Commercial notes and scientific information on essential oils.

Almond Oil, from apricot-kernels. Owing to the high prices of bitter almonds, the interest of speculators has in the course of the summer turned towards the Syrian apricot-kernels, and in view of the reports of a failure of the harvest in California, they succeeded in driving up last year's prices of about 60 marks, until they reached 80 marks per 100 kilos. The upward movement was promoted this time more particularly from Hamburg, and the fact that only small parcels of last year's harvest were available for the consumption was duly taken advantage of. Unfortunately, it would appear that cool heads regulating their operations in accordance with the reports on the new harvest, were absent, for it is obvious that otherwise the first supplies of new kernels would not have been taken up with such avidity. All information from the producing districts in Syria points to the fact that the result of this year's harvest may be called exceptionally abundant, and it may therefore be assumed as probable that the quotations will return again to a normal level, as soon as the first voracious appetite of the purchasers has been satisfied. It is only natural that the Syrian peasants are well pleased with the high prices, and that only by patiently holding out it will be possible to bring them to reason. In consequence of the numerous sensational reports spread from Hamburg, the demand for oil pressed from apricot-kernels was very brisk, and the prices advanced in proportion, but it is hoped that the latter may soon go back again.

Essential oil of bitter almonds could scarcely be procured in sufficient quantities also in the course of the past half-year, and it is therefore not surprising that our laboratory-journals show numerous cases of coarse adulterations.

Almond Oil, pressed from sweet almonds. The sweet almonds originating from Puglia and Sicily have during this summer

also become an object of speculation, for, although the trees had suffered greatly from bad weather in April, the consequent shortness in the result of the harvest cannot have been the only cause of the upward movement which finally brought the price of this article to about 180 marks, against 125 marks in the previous year. Our quotations of the newly pressed product had to be raised in proportion to the increased market-price of the raw material.

Angelica Oil. According to our experience, the Thuringian oils of angelica-root show in their properties some deviations from the distillates prepared by ourselves. The cause of the disparity, which is characterised by a comparatively low specific gravity and high rotatory power, may possibly be found in the less perfect distilling plant of the rural producers. We observed in Thuringian oils, as the lowest value of the specific gravity, 0,8542 (15°), and as the highest rotation $\alpha_D + 36° 10'$. On the other hand, the constants of the distillates produced by us lay within the following limits: $d_{15°}$ 0,8659 to 0,8736; $\alpha_D + 24° 2'$ to $+ 32° 35'$.

Anise Oil. The reports on this year's anise-harvest in Russia vary very considerably. Whilst from one quarter the results are characterised quantitatively as favourable, other informants state that the fields have greatly suffered from hail-storms and heavy rains, and that in consequence the result cannot be called satisfactory. Yet the reports almost throughout agree in this, that the seed is small and dark-coloured. As might be expected, in view of the continued unrest, many interested parties have refrained this year for obvious reasons from visiting the market which was held at Krasnoje on September 10th, so that the reports received on the progress of the latter do not allow of a correct view of the actual state of the market. On the whole, many complaints are heard about the quality, as the anise, owing to the rain, turns out very dark, and moreover is said to give a yield of oil equal to only two-thirds of that of last year. In consequence of the lack of visitors, business at Krasnoje was very dull, the more so, as the few buyers present assumed an attitude of expectancy. Since then, the Russian oil producers have raised their quotations of anise oil and of anethol, which shows that they are by no means satisfied with the harvest.

It is stated that this year about 4800 desjatins have been under cultivation, against 4000 last year, and the average result is estimated at about 30 pood per desjatin. The total crop would therefore amount to about 140000 pood, or about 20000 pood more than in 1905. In face of this splendid result, the firm tendency must be attributed solely to the deficiency in the quality. The news received from the second aniseed-market confirm on the whole the foregoing report, although the quality of the seed then offered was less defective.

The anise harvest in Spain has given excellent results, but for our branch of manufacture this quality does not come under consideration, on account of its high price.

The French firm in Bulgaria, of which we mentioned in our April Report that it intended taking up the distillation of Bulgarian anise on a large scale, has so far been unsuccessful, as the result this year has only been unimportant, and cannot enter into competition owing to the high cost-price.

We have in these pages repeatedly referred to the complaints[1]) made from the side of the German chemists about the use of anethol for *liq. ammon. anis.* It is, namely, said, that the substitution of anethol for anise oil is the cause of drawbacks which had not been observed before, inasmuch as when *liq. ammon. anis.* is added to liquid remedies, the anethol gradually separates out again, and collects in the form of scaly, closely concentrated masses on the surface of the mixture; similar conditions occur in the preparation of *elixir e succ. liquir.*

Now it has recently been pointed out in the pharmaceutical press[2]), in discussing this matter, that in order to remove the drawbacks mentioned above, the prescription of *liq. ammon. anis.* should be amended, for example by increasing the proportion of alcohol, or else that while the present composition of the liquor is maintained, the use of anise oil should again be fallen back upon.

We agree with this proposal in so far as it relates to the modification of the proportionate quantities of the *liq. ammon. anis.* and on the receipt of complaints addressed direct by to us we have also repeatedly laid stress on this. But the re-substitution of anise oil in the place of anethol would probably not lead to the end in view, as experiments have shown us that with the present superior quality of anise oil, the drawbacks are exactly the same as when pure anethol is used. The anise oil produced at the present time is of much better quality and has a larger anethol-content than that of former years, and this has naturally to be taken into consideration when the conditions in question are discussed. If for *liq. ammon. anis.* the present composition is maintained, the defects observed will remain, no matter whether anethol or anise oil is used in the preparation of the liquor.

A report in the pharmaceutical monthly notes of the Pharm. Zeitung[3]) dealing with the article quoted by us, requires correction on this point, that we have never maintained or proved that the

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[1]) Report October **1902**, 10; October **1904**, 10.
[2]) Pharm. Ztg. **51** (1906), 555.
[3]) Pharm. Ztg. **51** (1906), 612.

defects mentioned may also be caused by oxidation, or polymerisation processes. On the contrary, by the experiments[1]) which we made at the time and which we have also published, we have proved that such changes render the anethol more readily soluble, and for this reason cannot be the cause of the separation.

In a subsequent article in the Apotheker-Zeitung[2]) which deals with the same subject, the proposal is made to embody the anethol in the *elixir e succo liquiritiae* by emulsifying with gum acacia, possibly with the addition of a little *Paraffinum liquidum*, and also to keep the *liq. ammon. anis.* in stock as an emulsion for the purpose of dispensing.

Oil of Backhousia citriodora. This oil which has already been mentioned repeatedly in our Reports[3]), has lately also been examined by J. C. Umney and C. T. Bennett[4]), who found the following values: d_{15° 0,895 to 0,896; $\alpha_D \pm 0^\circ$ or very faintly to the left; aldehyde-content (chiefly citral) 94 to 95%, determined by the bisulphite method. The oil is soluble in ½ to 3 vol. 70 per cent. alcohol, and distils almost entirely between 215 and 230°. It is practically free from terpenes, but appears to contain traces of other bodies which impart to it its characteristic odour. The first 10% of the distillate had a penetrating odour like amyl ester, which the authors propose to submit to a further study. The residue had a high index of refraction pointing to the presence of traces of sesquiterpenes.

An oil recently examined by us had the following constants: d_{15° 0,8996; $\alpha_D \pm 0^\circ$; soluble in about 9 vol. 60 per cent. alcohol; aldehyde-content (determined with bisulphite) 96,5 to 97,0%; n_{D20° 1,48604.

Basil Oil. Our earnest endeavours to do away with the scarcity of this oil so highly valued by many perfumers have unfortunately for the present remained without result, in so far as it was not possible to discover either in France or Réunion any quantities worth mentioning, and as our own cultivation only supplied some few hundred grams which of course are of no account in view of the numerous orders still to be executed. Next year we shall have sufficient distillation material at our disposal to meet also larger requirements.

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[1]) Report October **1904**, 10 and 42.

[2]) Apotheker Ztg. **21** (1906), 613. A few errors occurring in this article may here be corrected: the sol. p. of pure anethol lies betwen 21 and 22°, that of anise oil not at + 14°, but above + 17°; Russian anise oil is moreover mentioned in a manner as if it were inferior to oils of other origin, whereas in reality Russian anise oil is particularly valued.

[3]) Bericht April **1888**, 20 and Report April **1905**, 83; comp. also Gildemeister and Hoffmann, The Volatile Oils, p. 538.

[4]) Chemist and Druggist **68** (1906), 738.

We determined in our oil the following properties: d_{15° 0,9038; α_D — 9° 15′; n_{D20° 1,48132; acid no. 21; ester no. 11,6; soluble in 1,5 and more vol. 80 per cent. alcohol, with separation of small crystals of paraffin.

Cade Oil. It is well known that genuine cade oil (*Oleum cadinum, Oleum juniperi empyreumaticum*) is derived from *Juniperus oxycedrus* L., which is chiefly indigenous to the countries of the Mediterranean and the Carpathians. But as the oils examined frequently admitted doubt of their origin, C. Pépin[1]) has traced some oils obtained from St. Sauveur, Var and Gard in the South of France, that is to say districts in which the cade oil is actually distilled from *Juniperus oxycedrus* L. The distillation is there carried on from September to May, and the distillation product is best left standing for 2 to 3 weeks. Of the three layers formed, only the upper one contains the oil which has a less specific gravity than water, and which should possess a brown-red colour and a distinct smoky odour. A simple reaction for distinguishing cade oil from pine tar oils, etc., is the following: 1 cc. of the oil to be examined is strongly shaken with 15 cc. petroleum ether and filtered; 10 cc. of the filtrate are mixed with an equal volume of a neutral 5 per cent. solution of copper acetate, again shaken, and the mixture left standing for some time; 5 cc. of the layer of petroleum ether are then removed with a siphon, and mixed with double the volume ethyl ether; this mixture acquires an intense green colour if the cade oil is adulterated with pine tar. In the case of genuine cade oil, only a feeble yellow-brown coloration occurs. According to Pépin it is possible to detect by means of this reaction, adulterations with down to 10 % pine tar.

Cajeput Oil. The normal conditions of this article, to which we could refer in the spring, did not, unfortunately, continue, for a scarcity has during the last few months become noticeable on the European markets, which was bound to find expression in a considerable advance in the prices. As will be seen from the table below, no direct shipments to Europe have been made during the first five months, and the exports to Singapore and Java appear to have found their way chiefly to the principal consuming country, the United States. The belief already mentioned before, that the consumption in Europe is on the decline, has since been confirmed by further experience. In many cases, where formerly cajeput oil was employed, the cheaper eucalyptus oils, which have a precisely similar action, are now used.

The shipments from Macassar during the first months are as follows (in cases of 25 bottles each): —

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[1]) Journ. de Chim. et Pharm. VI. **24** (1906), 49.

	Europe	America	Singapore	Java	China
January . .	—	—	70	240	—
February .	—	250	64	18	—
March . .	—	—	60	115	—
April . . .	—	—	28	191	25
May . . .	—	—	20	570	10
June . . .	110	—	60	428	—
July . . .	22	50	—	181	2

We have recently entered into relations with a grower in the producing island Buru, who promises to supply us from now with abundant oil of excellent quality. A not inconsiderable proportion of our purchases is also intended for export to America.

From Melbourne we received a sample of an oil distilled from the leaves of *Melaleuca linariifolia* Sm.[1]). The colourless distillate had a peculiar aromatic odour; d_{15° 0,9109; $\alpha_D + 3^\circ$; soluble in 1,5 vol. and more 80 per cent. alcohol; when more than 3 vol. are used, opalescence occurs. It contains considerable quantities of cineol, and in addition to this an aldehyde could be abstracted from the oil, which is probably identical with citronellal; the quantity of oil at our disposal was unfortunately so small, that a chemical proof in support of this could not be supplied.

Oil of Calamintha Nepeta. Through the kind assistance of a business friend we received 2 kilos of an oil from the herb of *Calamintha nepeta* Clairv., which, as mentioned by us on a previous occasion[2]), is placed on the market from the South of France under the unsuitable name "Essence marjolaine", and of whose composition we gave on the same occasion detailed information based on the work of Genvresse and Chablay[3]). The oil examined by us had a bright, greenish-yellow colour, and a mint-like odour; d_{15° 0,9271; $\alpha_D + 6^\circ 49'$; ester no. 13,0; soluble in 2,7 vol. and more 70 per cent. alcohol. On distillation *in vacuo* (5 mm.), the following fractions were obtained: —

1. (first runnings)	—50°	6,7 %	$\alpha_D - 16^\circ 0'$	d_{15° 0,8802
2.	50—75°	4,5 %	„ $- 44^\circ 0'$	„ 0,8229
3.	75—81°	5,8 %	„ $+ 2^\circ 56'$	„ 0,9057
4.	81—84°	29,6 %	„ $+ 15^\circ 55'$	„ 0,9241
5.	85—86°	36,85 %	„ $+ 16^\circ 0'$	„ 0,9374
6. (residue)		5,0 %	—	„ 0,9962

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1) Comp. Gildemeister and Hoffmann, The Volatile Oils, p. 523.
2) Report April **1903**, 50.
3) Compt. rend. **136** (1903), 387.

We paid particular attention to the new ketone discovered by Genvresse and Chablay in a fraction boiling at 208 to 209°, which the authors had isolated by means of the bisulphite compound, and to which they had given the name of calaminthone. For this purpose the fractions 3 and 4 were once more distilled at ordinary pressure, and the portions passing over at 208 to 209° collected for a thorough examination. Our researches, however, led to a distinctly different result; although we also succeeded in isolating a ketone with bisulphite, we regenerated from the bisulphite compound obtained only pulegone which we were able to identify by its semicarbazone of the m. p. 172°. But in addition to this there was present in the calaminthone fraction in question, a second ketone which could not be combined either with neutral or with acid sulphite. In order to separate the two bodies the fraction was freed from pulegone by repeated treatment with sodium sulphite, and in the ketone which had not entered into reaction, l-menthone was recognised with certainty. Its semicarbazone, after repeated recrystallisation, melted distinctly at 184°, its oxime at 59°.

According to these results it is probable that the ketone which Genvresse and Chablay called calaminthone, is not a uniform body, but a mixture of pulegone and menthone.

Camphor Oil. The scarcity of this oil (which is so important for our industry) has increased in a marked degree since we published our last Report, so that it is necessary to regard its future with serious apprehension. The deliveries of red camphor oil in Formosa are said to have been so unimportant in the last few months, that the demands of the Direction of the Monopoly could hardly be satisfied, — much less even a moderate quantity becomes available for export. For white oil the demand was so brisk from the Japanese industry (which in the course of time has also been able to make use of this article for their purposes), that the export of any quantities worth mentioning was out of the question. Whatever quantity of these two sorts was shipped to Europe and the United States in the course of the last few months, originates therefore from unexpired contracts.

The value of the camphor oil shipped from Japan in the first six months of this year amounted only to 71102 yen, in spite of the much higher prices, against 131007 yen in the same period of last year.

The following summary which has been taken from the Reports of the British Foreign Office (Ann. Series No. 3675) gives further information on the export of camphor to the individual principal consuming countries in the last three years. The value of the total shipments has fallen off in that time by nearly £ 100000, in spite of the higher market.

	India	France	Germany	United States	United Kingdom	Tota
	£	£	£	£	£	£
1905	53 000	58 000	12 000	100 000	26 000	262 000
1904	82 000	71 000	15 000	128 000	8 000	323 000
1903	61 000	37 000	68 000	117 000	50 000	361 154

The deficiency in the Formosa production appears to be chiefly due to the indiscriminate cutting-down of the trees which has taken place there during the last few years, and which must have caused considerable damage to the camphor-forests. This seems to be borne out by a proclamation issued in June of this year by the Governor-general of Formosa, General Sakuma, in which the peasants were strongly urged to devote their attention more to the camphor production, and to improve and extend as much as possible by new cultivation the plantation which had greatly suffered from the system of irrational exploitation hitherto in vogue. The proclamation also mentions that new cultivations covering an area of 1500 ko (1 ko = about $2^1/_2$ acres) have been commenced, and that it was intended to extend these, provided the Government received the necessary support from the peasants. How much time will elapse before these new forests are productive, and whether the call on the peasants will meet at all with a sympathetic response, it is of course at present impossible to say.

The following translation of an article which appeared in the "Taiwan Nichi Nichi Shimpo" (Formosa Daily News) of the 1st of February and was forwarded by the British Consul at Tamsui, may be of interest to persons dealing in camphor.

The previous prices, which have now been increased, were as follows (per picul = $133^1/_3$ lbs.): —

District	Crystallised camphor			Camphor oil
	1st grade	2nd grade	3rd grade	
	Yen	Yen	Yen	Yen
Gilan, Shinko, Toyen, Shinchiku, Bioritsu, Taichu, Nanto, Toroku	30,00	27,00	24,30	15,00
Kagi	31,00	28,00	25,30	15,50
Taito	32,70	29,70	27,00	16,30

There was great shortage in the production last year, and as the more easily accessible trees have nearly all been cut down, and the head-hunters still continue to make attacks on unprotected workers who advance too far into the camphor-forests, the Monopoly Bureau thought it advisable to stimulate producers and giving them better protection against the savages.

The Monopoly Bureau and their selling agents, Messrs. Samuel, Samuel & Co., have not disclosed whether any difference has been made in the price at which the camphor is handed over to them.

The camphor oil is all sent to the refineries in Japan, where about 49% of camphor is extracted from it.

A sketch-map accompanied this despatch, showing the Formosa districts mentioned herein.

Extract from "Nichi Nichi Shimpo" (Formosa Daily News).

Hitherto, with the exception of what comes from distant places, like Taito and Kagi, the Government have bought camphor and camphor oil at the same price, although from different places, with the result that producers have gained or lost according to the circumstances and locality of production and in some districts the camphor worker has obtained practically no profits at all.

The Government therefore have now taken this matter into consideration and have decided to alter the purchase-price in accordance with the conditions prevailing in each one of the various producing districts throughout the Island; this has resulted in an increase all round on previous prices, and the following table shows the increase in the present compared with the former prices for camphor and camphor oil.

Delivered at Taihoku per picul ($133^1/_3$ lbs.).

Camphor same for 1st, 2nd and 3rd grades			Camphor oil	
Gilan	increase of yen = $(2/0^1/_2)$	3,40	Increase of yen . . .	1,60
Shinko (1 part)	„	0,90	„ „ „ . . .	0,20
„ other part	„	2,70	„ „ „ . . .	1,10
Toyen (1 part)	„	0,50	No alteration.	
„ other part	„	3,10	Increase of yen . . .	1,20
Shinchiku	„	6,60	„ „ „ . . .	3,10
Byoritsu	„	2,30	„ „ „ . . .	0,90
Taichu (1 part)	„	3,10	„ „ „ . . .	1,20
„ other part	„	1,60	„ „ „ . . .	0,60
Nauto	„	1,60	„ „ „ . . .	0,60
Toroku (1 part)	„	1,20	„ „ „ . . .	0,30
„ other part	„	1,50	„ „ „ . . .	0,50
Kagi	„	4,50	„ „ „ . . .	2,00
Taito	„	1,20	„ „ „ . . .	0,40

The largest increase amongst the above is that for Shinchiku, which shows camphor (yen) 6,60 and camphor oil (yen) 3,10, the difference in the increase for several districts varies in accordance with the richness of the material, the cost of transport, the accessibility of the

camphor forests, the cost of labour and the cost of living, etc., so as to allow of fair profits being obtained even in districts where very small quantities are produced. This result had previously not been obtained and it is therefore expected that even abandoned camphor districts will now once more be worked upon and that the total camphor production will be increased and the trees be handled more carefully. Furthermore, as a natural consequence of the increase in the purchasing price, the Monopoly Bureau will alter the selling price at which it hands over the camphor to Messrs. Samuel, Samuel & Co., the selling agents, and from the 10th inst. the price will be increased, so that the price at which Messrs. Samuel, Samuel & Co. sell abroad will also necessarily become higher, but it is not expected that an increase in Samuel, Samuel & Co.'s selling price will have very much effect on the market. The reason for this is that hitherto the selling agents have sold what they have bought from the Bureau within fixed limits, taking a certain percentage as commission, and that whereas the World's demand for camphor is nine or ten million pounds, the supply from Japan and Formosa is only 6 or 7 million pounds, so that as soon as the camphor leaves the selling agents' hands, it jumps up in price, and the difference between the market and Messrs. Samuel, Samuel's selling price is very great. Anyway the increase in the Government's buying and selling prices will probably result in large profits for the camphor industry."

With regard to the camphor producing districts of other countries, it is to be regretted that for the present no relief of the existing scarcity can be expected from that side. A report from the U. S. Consul in Amoy says that the camphor monopoly granted in 1903 to a Japanese Company for the Chinese province Fokien has been cancelled by the Government, after payment of a not inconsiderable indemnity, but that the Japanese even under the new conditions still control the production, and, as our own informants tell us, pay any price in order to secure every consignment.

The camphor production in Ceylon is unfortunately still in a very bad way, and although much attention has now for several years been given to this new cultivation, it has not yet been possible to produce actually more than about 1000 kilos. If it is taken into consideration that more than 900 acres are planted with camphor-trees, the result must be called unsatisfactory. The principal difficulty lies in the lack of experience of the planters in the distillation, and it is believed that the Japanese and Chinese make use of special technical artifices to secure a paying yield. It is said that the plantations will be extended further and it is hoped that the energy of Mr. Kelway Bamber, the Government chemist at Peradeniya, will succeed in overcoming the existing difficulties, and showing the planters

a remunerative method of manufacture. The present high prices of camphor are naturally very tempting, and it remains an open question whether the cultivation can still pay, if some day the camphor market returns to a normal level.

According to a report from the German Consul at Bombay, the Government, on the suggestion of the local Chamber of Commerce, has the intention of making experiments in the planting of camphor-trees in the Bombay district, and we hope on a later occasion to be able to return to the results of these experiments. The climatic conditions on the Indian coast agree approximately with those of Formosa, and in our opinion the prospects are therefore favourable.

M. Kimberlin reports in the "American Druggist and Pharmaceutical Record" (according to an article in the "Tropenpflanzer") on experiments in the cultivation of camphor-trees in California: —

> Camphor-trees have been found near Lake Shabot in the mountains situated sideways of Berkeley in Alameda county, Cal.; most of these trees are 20 to 35 years old, as can be ascertained from the annual rings. They belong to the species *Cinnamomum camphora*, from which the official camphor is obtained. They are over 25 ft. high; the trees have a large number of branches, a smooth bark, and green, broad, thick leaves pointed at both ends. The freshly peeled bark has an odour like sassafras. The trees grow in a heavy soil, have tapering trunks, with numerous roots which supply abundant nourishment to the tree. When the leaves are rubbed they emit a camphoraceous odour, which is also apparent in all the other parts of the tree. The wood, leaves and branches burn very readily, owing to their camphor-content. The camphor contained in them belongs to the class of general camphors ($C_{10}H_{16}O$) and is reckoned among the ketones.
>
> Experiments made with the wood of these Californian camphor-trees, when it was distilled with a little water, and on condensation of the vapours, actually resulted in a yield of camphor. The leaves contained about 0,15% camphor of great purity, purer than Japanese or Chinese camphor which must first be purified by refining. The camphor obtained by heating the wood of the Californian camphor-trees to a higher temperature, was not so pure as the product distilled from the leaves and branches.
>
> Camphor-trees were planted by the Department of Agriculture in many places, and have grown up to fine tall, green trees; they are more weather-resisting than orange-trees, for which they served to afford shade. Camphor-trees thrive in the climate of the coast, to the North of Charleston, in South Carolina, and along the Californian coast. It will be left to a later age to derive profit from the camphor-trees planted, as considerable quantities (annually about 6000) are planted out from the nurseries in suitable districts; but further experiments must show whether the leaves, branches, roots, or the wood of the trunk yield the best camphor, and what will be the most suitable season, the best method of distillation, etc.

On the occasion of the 6th International Congress for Applied Chemistry at Rome, Giglioli pointed out, in a paper on Italian camphor, that the camphor-tree thrives in almost every district of Italy, except in the neighbourhood of the Alps, and that it would therefore appear desirable to promote the cultivation of this tree in

Italy, the more so as it does not make a large demand on the soil. According to experiments made, the leaves of the tree are said to yield on the average about 1 % camphor, whilst the wood, which moreover lends itself exceptionally well for the manufacture of furniture, contains about 0,1 % camphor of inferior quality.

We have on several occasions, when discussing the camphor industry in our Reports, also referred in a more or less detailed manner to the cultivation of the camphor-tree[1]), and for this reason we wish to call attention to a most interesting article which deals with the observations made by C. Crévost[2]) with regard to the cultivation of the camphor-tree in Indo-China. In Tonquin, Kwang-Tcheou-Wan, and especially in Annam the cultivation of the camphor-tree justifies the most sanguine expectations. Various samples distilled by Aufray, the Director of the Tonquin laboratory, gave the following results as compared with Japan camphor (camphor oil + camphor):

	Japan	Tonquin	Kwang Tcheou-Wan
Ordinary branches . . .	3,70 %	3,90 %	3,25 %
Lower portion of trunk .	4,23 %	2,70 %	3,55 %
Roots	4,46 %	4,60 %	3,55 %

Contrary to the camphor-trees in Japan and in Kwang Tcheou-Wan, those in Tonquin always give a larger yield from the branches and roots than from the trunk. The yield mentioned in the table is, however, exceptionally very small, as the sample was taken from a hollow tree of very medium quality. The information given by Crévost dates already from the spring of 1904, and it may therefore be assumed that the experiments have since been extended. The solution of this question is too important to be neglected, and we hope to be able to return to the subject in our next Report.

From the Imperial Biologico-Agricultural Experimental Station Amani in German East Africa, we recently received a camphor oil which had been obtained in a yield of not quite 1 % by distillation of the leaves and branches of camphor-trees, respectively $2^1/_4$ and $1^1/_4$ years old. The oil sent to us was a filtrate of the original oil which separated off camphor spontaneously, and had the following properties: d_{15° 0,9236; $\alpha_D + 39^\circ 20'$; soluble in 0,25 vol. 90 per cent. and in 10 vol. 80 per cent. alcohol. The colour was golden yellow, and the odour differed considerably from that of ordinary camphor oil. When cooled, the oil congealed into a solid mass. By means of 4 % soda liquor, traces of a phenol were obtained which had an odour like

[1]) Reports October **1901**, 13; October **1904**, 15; April **1906**, 11.

[2]) Journal d'Agriculture tropicale **6** (1906), 105.

carvacrol, but could not be identified further. Eugenol which, as is well known, is present in the ordinary camphor oil usually obtained from the wood of the roots and the trunk, could not be detected. Neither did the oil contain alcohols (borneol) in any appreciable quantity; we found the acetylation number 14,5. The camphor-content of the oil as received by us was 75 %. It also differed from Japan oil by the absence of safrol. We attempted to detect this constituent by treating the oil several times with hydroxylamine in order to remove the camphor, and fractionating *in vacuo* the unchanged portion of the oil which had distilled over with the water vapour. But not one of the fractions boiling between 50° and 110° (7 to 8 mm. pressure) had even a remote odour of safrol. This difference in the composition of the two camphor oils in question may be due to this, that in the distillation of the oils the parts of the plant used were not the same.

Cananga Oil. In purchasing this oil, which is of such great importance for perfumery purposes, we specify the highest possible requirements, and as a consequence our stocks enjoy the constant approval of the leading experts. We have always at our disposal a considerable quantity, and are thus able to meet any demand.

Caraway Oil. In the spring months of this year the prospects of the caraway-harvest in Holland were very favourable, for according to official information the area cultivated with caraway was considerably larger than in 1905, and the reports on the condition of the plants were on the whole also satisfactory. North Holland, however, made an exception even at that time, as the dry summer of 1905 appeared to have had an injurious effect on the plants, and much damage was done especially by mice. Later reports though were already less hopeful. The germination had suffered during the flowering season through unfavourable weather and frost, and consequently left much to be desired in the principal districts, Groningen, Zealand, North Brabant and North Holland. According to the information published by the Dutch Government, the area cultivated with caraway was made up as follows: —

	1906	1905	1904
Groningen	2297 acres	1085 acres	2280 acres
Friesland	122 „	65 „	117 „
North Holland . . .	4682 „	5047 „	5237 „
South Holland	467 „	522 „	660 „
Zealand	1917 „	2057 „	2505 „
North Brabant . . .	1795 „	1925 „	2557 „
Totals:	11280 acres	10701 acres	13356 acre[s]

The condition of the fields at the commencement of the harvest was in figures[1]): —

for	Groningen	70
„	Friesland	70
„	North Holland	70
„	South Holland	55
„	Zealand	60
„	North Brabant	60 and 70

The yield of the harvest in bales per acre has not yet been officially determined, but in the chief districts it is estimated as follows:

Groningen	at about	8	bales per acre
North Holland	„	$7^1/_2$	„ „ „
Zealand	„	$6^1/_2$	„ „ „
North Brabant	„	7	„ „ „

so that an average yield of 7 bales per acre is believed to be correct.

The exports during the last 6 years were: —

in 1905:	4668534	kilos
1904:	6351154	„
1903:	5548568	„
1902:	5353567	„
1901:	7166600	„
1900:	4092245	„

that is to say, an average of 5530111 kilos per annum. At the accepted yield of 7 bales per acre, the production this year would only amount to 4061700 kilos, i. e. a deficiency of 1468411 kilos or 29368 bales.

These facts may show most clearly that the tendency of the market is very firm. As other producing districts, as far as reports have been received, hardly come under consideration as cover for the deficiency, it is possible that higher prices will soon have to be taken into account.

Cassia Oil. The prices of this important oil have risen considerably during October and high-quality oils are becoming very scarce. The quotations in China have risen from 3/3 to 4/2 c. f. & i., and it seems as if after a long interval speculation were going in for the article. Whether this firmer condition of the market is only temporary, or further surprises must be looked for, is at present impossible to say. The fact that our synthetic cinnamic aldehyde can

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[1]) 100 = excellent, 90 = very good, 70 = good, 60 = fairly good, 55 = middling, 40 = bad, 30 = very bad, 10 = failure of harvest.

always be had in any quantity, and possibly may be supplied some time even much cheaper than at present quoted, is a sufficient guarantee that prices of cassia oil, such as ruled towards the end of the nineties, need not be feared again.

Oil of Champaca-blossoms. After many fruitless and expensive attempts, we have at last succeeded in discovering a reliable source of supply of this oil which for a long time we had been compelled to omit from our lists. We expect shortly the arrival of several kilos, so that the scientific examination of this oil can now also be taken in hand.

The properties of the oil of the first consignment were: $d_{15°}$ 0,8861; α_D — 11° 10′; acid no. 10,0; ester no. 21,6; ester no. after acetylation 150,1; soluble in 2 vol. 70 per cent. alcohol; when 4 vol. and more are added, strong turbidity; soluble in 1 vol. and more 80 per cent. alcohol, when more than 7 vol. are added, opalescence (separation of paraffin). The oil has a bright brown colour and shows, especially in alcoholic solution, a very feeble blueish fluorescence, which may possibly be due to the presence of anthranilic acid ester. Of alcohols, linalool appears to be present in the oil, but owing to the small quantities of oil at our disposal, we were unable to obtain an exact proof of this.

Cinnamon Oil, Japan. K. Keimatsu[1]), in examining the essential oils from the leaves, trunks and roots of *Cinnamomum Loureirii* Nees, growing in the Japanese province Ki-i, found the following constituents. In the oil from the leaves: as principal constituent citral, and small quantities of eugenol; in the oil from the trunks: as principal constituent cinnamic aldehyde, and also small quantities of eugenol; in the oil from the roots: as principal constituent cinnamic aldehyde, and further camphene, cineol, and linalool. — These results agree with those of our own earlier examinations[2]), made with the oil from the twigs and leaves of the Japanese cinnamon or cassia bark tree, *C. Loureirii* Nees. We described the oil at the time as oil of nikkei.

Citronella Oil. The position of this important article can be judged only with difficulty, as reports on the conditions in the producing districts have lately been very scarce, and one has chiefly to depend on conjectures. It may be taken as a fact that all the oil shipped before the bursting of the monsoon, i. e. in October and November, will be absorbed by existing contracts; the unimportant quan-

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[1]) Journ. Pharm. of Japan **1906**, 105; accord. to Apotheker-Ztg. **21** (1906), 306.

[2]) Report October **1904**, 96; comp. Gildemeister and Hoffmann, The Volatile Oils, p. 391.

tities which arrive during the monsoon are too small to have any effect whatever on the market, and as the production in December and January is generally much smaller than the results of the July-September harvest, it is probable that speculative sales made in the meantime will not allow the market to become quiet.

The figures of the export from Ceylon up to 20th August are: —

$$\text{in } 1906,\ 694\,267 \text{ lbs. against } \begin{cases} \text{in } 1905,\ 855\,615 \text{ lbs.} \\ \text{in } 1904,\ 768\,660 \text{ ,,} \end{cases}$$

The shortage of about 160000 lbs. as compared with 1905 may therefore be the principal cause of the present firm state of the market, for the demand of the soap-industry is decidedly increasing, the more so as spike and lavender oils have long since become too expensive for cheap soaps. If, therefore, the shortage in the export increases towards the end of the year, there can be no doubt that in 1907 the prices will be considerably higher still.

We have at our disposal stocks of considerable quantities, proportionate to our sales of this article, and would ask buyers of large quantities to apply for our special quotations when in the market.

We were recently compelled to raise the price of the Java quality which is in great request, especially from the side of manufacturers of better-class soaps, as the producer under the existing conditions appeared not to make any profit out of it. The shipments during the last few months were also far from plentiful, and we are anxiously looking forward to the receipt of further news explaining the causes of this regrettable shortage.

We abstract the following details from a comprehensive article by A. Joyasuriya[1]) on the citronella oil industry which is of great importance for the inhabitants of Ceylon, as some 40000 acres are cultivated with citronella grass. Starting from the principle that the largest yield of oil at the smallest expense can only be attained by carrying out practical experiments on a scientific basis, Joyasuriya has made the most varied experiments, and has obtained results worthy of consideration, without being able to give an explanation of every single occurrence.

The history of the citronella plant is shrouded in darkness, and the most varied opinions prevail on the origin of the different varieties[2]). The mother-plant, as is well known, is *Andropogon Nardus* L.; the four different varieties which occur are separated into two groups: "maha-pangiri" and "lanabatu", of which each has its advantages and disadvantages. The former gives a rich yield of oil, which is greatly

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[1]) Oil, Paint and Drug Reporter 70 (1906), 25, and The Times of Ceylon of 3rd April, 1906.

[2]) Comp. Report April 1905, 55.

valued on account of a high content of aromatic substances; but the plant requires a comparatively rich soil and much care, as it has to be transplanted frequently. The "lanabatu" gives a smaller yield of oil, which is less aromatic, and consequently of less value; on the other hand, the plant thrives in a poor soil and does not require transplanting. As the bulk of the oil produced in Ceylon originates from "lanabatu", it is in Joyasuriya's opinion obvious that Ceylon citronella oil has a smaller commercial value than Java and Singapore citronella oil. This can in the author's opinion only be altered when "mahapangiri" is grown in Ceylon. In order to carry through such a radical measure which is necessary to reinstate the once flourishing industry, the Government should establish plantations of the better variety, and from these issue plants to the inhabitants on favourable terms.

Joyasuriya recommends for the cultivation that the plants should be fairly wide apart, say about 15000 per acre, and more attention should be paid to the drainage and the fertilisation of the soil, and also to the weeding. As it sometimes happens at the time of the rice harvest that plantations of citronella grass go entirely or partly to waste owing to the lack of cheap labour, it is advisable to introduce mowing machines so as to reduce the cost of production. For the distillation the freshly cut grass is not used, as it yields an oil with an unpleasant odour, but well-dried grass giving a pleasantly-smelling oil; when drying the grass, great care should be taken to prevent fermentation or rotting. The grass is cut either 4 or only 3 times annually; the latter is to be preferred. The yield of oil increases up to the third year of the plantation, and amounts to about 71 lbs. 3 ozs. per acre annually. After the third year the yield of oil diminishes constantly, although the grass looks very well.

The meteorological conditions have also a considerable influence on citronella grass. In the less highly situated districts, a good oil is obtained and a larger yield than the same plant would give at greater altitudes. Although Joyasuriya's observations are not complete, he obtained as a rule in higher-situated districts an inferior quality and smaller quantity of oil, which was not due to unfavourable conditions of the soil.

According to Joyasuriya's experience, adulterations are not responsible for the low price of Ceylon citronella oil; he seeks the cause in the inferior quality of the oil from the variety cultivated which yields an oil of less value, and also in over-production of oil. Contrary to this, the Java and Singapore oils fetch higher prices, as they are of better quality, due to the superiority of the variety of grass. If therefore it is desired to place the Ceylon oil and the other oils on an equal footing, it will be necessary to cultivate the better variety.

According to a paper by Wright[1]), endeavours are made to render the citronella industry more remunerative by using the grass from which the oil has been removed as raw material for the manufacture of paper, for which purpose it is said to be very suitable.

We need not enter more fully into the further details given by Wright on the valuation and judging of citronella oil, as these appear to be chiefly based upon the work of Sage, with which we have already dealt in our last Report[2]). We also consider that the content of total geraniol represents the principal factor in judging the value of citronella oil; but Schimmel's test, carried out by itself, will, according to our experience, always give useful data for a rapid test of the quality of a citronella oil.

Clove Oil. On the harvest of 1904/5 there is now available a Report from the British Vice-consul in Pemba, in which it is stated that no fewer than 755543 frasileh[3]), i. e. 227178 cwts., have been gathered. With this result, the harvest has, as far as statistical data go, far exceeded every former record. Of the above-named quantity, 675683 frasileh belong to Pemba, and only 79680 frasileh to Zanzibar itself. As might have been expected, the 1905/6 harvest in Pemba left something to be desired, for a rich crop is usually followed by a failure of the harvest. In Zanzibar, however, the harvest has given a medium result. The price, which at the beginning of 1905 came to 11/4 per frasileh for Zanzibar cloves, remained at that level until about May, and then gradually rose to 12/8, and subsequently in July-August to 18/8. In September a decline set in, and the quotations fell down to 16/- at the end of December. The average price for 1905 was 14/5½ for Zanzibar and 13/5½ for Pemba cloves. The fluctuations in the prices were chiefly due to speculative enterprise in England and India.

The total value of the export in 1905 was £ 287073; of this, the individual principal consuming countries received supplies of the following values: —

United Kingdom .	£ 54709,	against	£ 119913	in 1904
British India . . .	132236	„	98454	„
Holland	36992	„	24866	„
America	32735	„	47651	„
Germany	12089	„	9221	„
France	3615	„	16274	„
Austria-Hungary .	2573	„	3944	„

1) The Times of Ceylon, April 3, **1906**.
2) Report April **1906**, 19.
3) Comp. estimate by the German Consul at Zanzibar. Report April **1906**, 21.

The stocks on the principal markets on 1st September were: —

	Holland	London	New York	Total	
1900	77000	21500	14700	113200	bales
1901	64500	16300	13900	94700	„
1902	54500	16000	10800	81300	„
1903	33500	17400	8000	58900	„
1904	5200	19000	4000	28200	„
1905	9200	26000	7000	42200	„
1906	5900	25000	2000	32900	„

The last six harvests gave the following results: —

1900/1 . . .	65000	bales
1901/2 . . .	90000	„
1902/3 . . .	105000	„
1903/4 . . .	35000	„
1904/5 . . .	185000	„
1905/6 . . .	65000	„

Reports on the 1906/7 harvest differ, but on the whole are not favourable, and we are inclined to believe that for the next 12 months, i. e. up to the time when the result of the season of 1907/8 becomes available, the prices will rule high. The estimates vary between 30000 and 120000 bales, and the mean of 75000 bales may probably be nearest the truth. The tone at Amsterdam and London is very pessimistic, though at Hamburg the situation is considered better. The small stocks on 1st September, 1906, quoted above, give, however, food for thought. Now, as before, the attitude of the speculators will probably be decisive.

Clove-stems could only be obtained with difficulty in the last few months, and for this material also higher prices had to be paid. Lately the sellers have partly retired entirely from the market.

In what unheard-of manner adulteration still frequently takes place, is shown by the following examination of a clove oil which was sent to us from Bohemia for an expression of opinion. The suspicion of the purchaser aroused by the abnormally low price of the oil was completely justified; the only thing to admire is the daring with which a merchant ventures to place such a coarsely adulterated oil on the market. The oil behaved as follows: d_{15° 0,9686; α_D — 51° 14′; about 32 % eugenol; not soluble in 10 vol. 90 per cent. alcohol; miscible with 95 per cent. alcohol. The non-phenols consisted, according to a more detailed examination, chiefly of gurjun balsam oil, and showed the following constants: d_{15° 0,9234; α_D — 79° 52′; soluble in 7 and more vol. 95 per cent. alcohol. According to these results, the clove oil had been mixed with about 60 % gurjun balsam oil.

Oil of Copaiba. Utz[1]) has made comparative experiments with regard to the determination of the saponification number of copaiba balsam by cold and hot process, and has found that in this case, contrary to Peru balsam[2]) the "saponification number cold" frequently remains behind the "saponification number hot". With the saponification number (cold) previously ascertained by K. Dieterich[3]), only those found with Angostura balsam agreed, whilst with Maracaibo balsam and Para balsam, Utz obtained higher values. From this Utz concludes that the balsams in question were adulterated. If he also mentions that, according to Dieterich, among others gurjun balsam also raises the saponification number, this is an error of Dieterich's, as gurjun balsam has a very low saponification number (about 6 to 26), and could only have the effect of lowering, and not raising, the saponification number of copaiba balsam. For the rest, this also follows from the table[4]) given by Dieterich under Maracaibo balsam. — We would still mention that the sapon. nos. of three copaiba balsams, determined by us some time ago by cold process, were throughout somewhat higher than those found by hot process.[5])

L. van Itallie and C. H. Nieuwland[6]) have again examined Surinam copaiba balsam, without however, as the authors themselves state, adding much to our knowledge of this drug. The separation of the resin acids obtained by the usual method, by fractional precipitation or distillation, led to no result. The sesquiterpene alcohol (m. p. 114 to 115°) contained in the oil, which had already been detected previously, gives a sesquiterpene with the following constants: d_{15° 0,952; n_{D15° 1,5189; b. p. 252° (759 mm. pressure); α_D —61,7°. With regard to the colour-reaction of copaiba balsam with acetic anhydride and sulphuric acid[7]), the authors found with the samples which we had placed at their disposal, that Para balsam gave a dark blue green, subsequently dark blue violet, Bahia balsam a blue, and Angostura balsam a dark-violet coloration, which is an additional proof that not much reliance can be placed on colour-reactions.

Coriander Oil. According to the information received, the Russian coriander harvest has given excellent results, and an abundant

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1) Apotheker-Ztg. **21** (1906), 205.

2) In the case of Peru balsam, the sapon. nos. ascertained by cold process were in every case higher (by about 3 to 22) than those determined by hot process, which agrees with Dieterich's observations.

3) K. Dieterich, Analyse der Harze, Balsame und Gummiharze, pp. 55 and 99.

4) Ibidem p. 63.

5) Report April **1905**, 32.

6) Arch. der Pharm. **244** (1906), 161. Acc. to Pharm. Weekblad **43** (1906), 389; comp. also Report April **1905**, 25.

7) loc. cit.

supply of distillation material will be available from this source. Yet at present it seems at least doubtful that the prices will return to the former reasonable level, as certain speculators use every effort to support the market. On the other hand, Russian coriander oil of this year's distillation has already been offered from a reliable source at 50 marks per kilo. As fairly large quantities of last year's (and therefore more expensive) stocks appear still to be held, it is probable that a similar quotation here is for the present out of the question. From Moravia, coriander is also offered abundantly and in good quality. The remunerative prices of 1905 appear to have induced many farmers to apply themselves with particular energy to the cultivation of coriander.

Owing to its high price, coriander oil is frequently the subject of adulteration; quite recently such a product was again submitted to us for approval, which had the following properties: d_{15° 0,8752; $\alpha_D + 33^\circ 29'$; sap. no. 5,5; insoluble in 10 vol. 70 per cent. alcohol. The high rotation and also the insolubility in 70 per cent. alcohol characterise the oil at once as adulterated; probably several substances had been added in this case, but we found it impossible to determine their character, as the sample received by us was insufficient for the purpose. For comparison we add here the properties of pure coriander oil; d_{15° 0,870 to 0,885; $\alpha_D + 8^\circ$ to $+ 13^\circ$; sap. no. 4,0 to 23,0; soluble in 2 to 3 and more vol. 70 per cent. alcohol.

Elemi Oil. The last communication from A. Vesterberg[1]) on Manila elemi resin dates from 1891. In a publication[2]) now before us, the some author has detected in the resin a secondary alcohol which perhaps for this reason excites greater interest, that it is the first known di-valent resin alcohol. The bulk of the crystallising substances of elemi resin, as is well known, consists of amyrin, but in addition to this Baup[3]) had already determined three other crystallising substances, breïne, breïdine, and bryoïdine. Vesterberg now believes to have characterised the first. The melting point lies about 216 to 217° (not corr.), $[\alpha]_D$ in alcoholic solution $+ 65{,}5^\circ$. Breïne is a pronounced divalent alcohol of the as yet doubtful formula $C_{30}H_{48}(OH)_2$, and yields with acetic anhydride a diacetyl derivative, from which it can be regenerated by saponification with alcoholic potash.

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[1]) Berl. Berichte **24** (1891), 3834, 3836; ibidem **20** (1887), 1242; **23** (1890), 3186.

[2]) Berl. Berichte **39** (1906), 2467.

[3]) Jahresbericht für Chemie **1851**, 528.

Essential oils, Sicilian and Calabrian.

Our esteemed friend, Mr. Eduardo Jacob of Messina, reports to us under date of 6th September, as follows: —

In my spring report I was already able to say that the export of our essential oils, as compared with that of last year, had increased not inconsiderably during the first two months. This increase has continued, and only the high prices of the last two months have led to a slackening of the export. It is interesting to compare this year's figures with those of last year.

The export amounted: —

		1906	1905	1904
in January	to kilos	109392	89548	105877
„ February	„ „	83300	80780	98897
„ March	„ „	85294	80157	91132
„ April	„ „	80167	68657	74955
„ May	„ „	96571	53032	57932
„ June	„ „	75046	59726	84286
„ July	„ „	39396	47219	52586
„ August	„ „	27184	43339	47074
	Total kilos	596350	532458	612737

The present export is therefore but little short of that of 1904, which year (leaving 1902 out of the question) shows the highest export figures. The lion's share of the increase of 63892 kilos, viz., 36947 kilos, belongs to the export to the United States.

The progress of the trade in the individual essential oils is represented by the following: —

Bergamot Oil. The brisk business in the first months of this year had prevented the accumulation of very large stocks locally, so that the proprietors were in a position to sell their goods on the market at a continuously firm price, without, however, thereby causing any important advance; the prices only rose during the four months March, April, May and June by about 1 mark, from 17,50 to 18,50 marks.

In July, however, a decisive change came over the market. On the one hand the stocks had meanwhile dwindled down very much, and on the other the reports about the prospects of the harvest began to assume a disconcerting tone. Under the influence of these reports the owners of prompt oil first of all held off entirely, and then, after about a week, appeared on the market demanding prices which were from 1 to 1,50 marks higher. Although the purchasers at first refused to pay these prices of 19,50 to 19,75 marks, they were soon compelled to give in, and after a short time a very brisk trade developed at advancing prices, which meanwhile had risen to 20,50 marks.

As the stocks of old oil on hand are estimated at not more than 3000 kilos, and as moreover the new harvest will probably start with high prices, all the conditions favour a continued firmness in this article, and if the demand from abroad continues as at present, a further advance in the prices would not by any means be impossible, or even improbable.

As already mentioned above, the prospects of the new harvest are very bad, in spite of the fact that the trees have blossomed very abundantly in the spring. It has once more been proved that the trees are not capable of producing two good crops one after the other; after last year's rich harvest, the trees were this spring no longer able to convert the wealth of blossoms into fruit, and in May and chiefly in June the young fruits dropped off in large numbers, so that at present the coming crop is estimated at barely half that of last year. The proprietors of the gardens are consequently very reserved, and not inclined to any forward sales. The new manufacturing season will therefore probably commence with very high prices, which will move approximately on the basis of 20 marks. The subsequent movement of the price will then depend essentially upon the greater or smaller demand from abroad. As it may be assumed that the foreign consumers, owing to the heavy export of bergamot oil in the course of this year, are now generally well supplied with oil, it is possible that this may put a limit to the exaggerated demands of the manufacturers of bergamot oil.

Lemon Oil. This article has during the last six months passed through such stormy and excited times, as probably never before to such an extent. Whilst in April the prices stood at 5,80 marks, they have since risen to 11,25 marks, at which level they have now for some time firmly maintained themselves.

The reasons of this exceptionally large increase in the prices are various. In my spring report I already expressed the fear that the quantities of oil produced in the last manufacturing season would barely suffice to meet the world's consumption, and this fear has been completely realised, as the whole of the oil at present still in Sicily is estimated at scarcely 15000 kilos, such a small quantity, that under normal conditions it would not cover the demand of one single autumn month.

Another occurrence which contributed towards the rise was the fact, which became apparent at the commencement of the upward movement, that several large export firms in our town had made uncovered sales abroad for very large quantities of lemon oil, and were now compelled to appear on the market with a strong demand whilst prices independently of this were advancing. This commenced in the first days of May, when the prices had risen to 6,15 marks; in the course of that month they reached the level of 6,50 marks, and then

then advanced by leaps and bounds in June to 8,50 marks and in July to over 11,00 marks, at which level they still stand.

It is clear that even heavy uncovered contracts would not readily have led to such an unheard-of advance in the prices, if the general conditions had not favoured the movement, inasmuch as the manufacturers of lemon oil and citrate of lime, owing to the favourable development of the trade in these two articles, were abundantly supplied with means which enabled them to take full advantage of the market, and by very cleverly supporting it with always comparatively small quantities of marketable oil forced the buyers (who already had the knife at the throat) to pay constantly increasing prices. But a further fact has hereby also come to the light, and one which had not been expected in such a degree, namely that in spite of the decidedly larger exports of oil as compared with the previous year, no large stocks of lemon oil had accumulated abroad; notwithstanding the surprisingly rapid advance in the prices, a very animated demand arose from the side of foreign buyers who were compelled, whether they liked it or not, to pay the high prices of the day.

When forming an opinion of the probable movement of the prices of this article during the next few months, until the new essence comes in, various circumstances have to be taken into consideration. On the one hand, it goes without saying that both the local and the foreign consumers in view of the high prices ruling have cut down their purchases to the lowest limits, and will endeavour to restrict them further until the time of the new harvest; on the other hand, there is no doubt that a large quantity is still uncovered locally which has to be satisfied before the new harvest, so that in any case a very brisk demand will hardly be wanting. Now if it is considered that even the most liberal estimates of the stocks in the hands of manufacturers, speculators and exporters, as already mentioned, do not exceed barely 15000 kilos, and that this has to meet the requirements for quite three months, one cannot shut one's eyes to the fact that a decline of the prices cannot be hoped for, but that it is very well possible, if not to say probable, that several orders to buy arriving at the same time will easily drive the prices up still further.

A matter which should not be left unsaid is that the adulteration of lemon oil at the present high prices has lately again acquired larger dimensions, as many exporters endeavour to reduce in this manner their loss on earlier cheap contracts for forward delivery.

Under the present circumstances it is particularly important to form a clear notion of the presumable movement of the price of essence during the coming manufacturing season.

In the first place, with regard to the conditions of the harvest, the reports from the various districts differ very considerably. Whilst

the crop in the large producing districts on the North coast of Sicily is estimated at about 15 % less than that of last year, the lemon gardens on the East coast appear to promise a better result, so that the total harvest is on the average estimated as approximately the same as that of the previous year. But it should not be lost sight of that especially on the East coast the first blossom has been less good, and consequently a large proportion of the fruit now on the trees will only come in for the later manufacturing months.

It is further taken into consideration that in the coming winter the lemons will for the first time be admitted free of duty into Germany, and that this in all probability will have the effect of withdrawing a large quantity of fruit from the manufacture of essence.

Finally it is natural that in the first months of the manufacturing season the market will be flooded with a particularly brisk demand for lemon oil from abroad, where only very small stocks can exist, and that to satisfy this demand only a comparatively small quantity of free oil will be available. Quite exceptionally large purchases for forward delivery, at prices of 7,25 to 7,50 marks, have namely been made here by a few speculators and by the Union of manufacturers of citrate of lime and lemon oil, to which I have already repeatedly referred in my previous reports, and the former — all people with plenty of capital — as well as the latter, will in any case only place their oil slowly and carefully on the market, so that the market will never suffer from a glut.

Under these conditions it is hardly possible to err when assuming that the prices of lemon oil in the first months of the manufacturing season will remain at the basis of about 7,25 to 7,75 marks, and in the first few weeks of November will certainly go a good deal higher still. How the oil market will subsequently shape itself will then depend chiefly upon the movement of the trade in lemons in cases, and upon the steps which the Union may take. But a return to the former very cheap prices appears out of the question, if it is considered that in spite of last year's favourable manufacturing conditions, there was not sufficient oil at disposal to satisfy the world's consumption without a violent convulsion of the market.

Mandarin Oil. The old oil has been almost entirely used up, and the small parcels which change hands here fetch about 33,50 marks.

The new harvest appears unfortunately to turn out very bad. The trees which last year produced a rich crop, now carry very little fruit, and the latter is small and undeveloped owing to the continuous drought. In consequence of this the new manufacturing season will probably set in with prices at about 32 marks.

Orange Oil, bitter. The transactions in this oil have been comparatively small; the prices which in the spring months stood at 17 marks, gradually declined with insufficient demand, and reached their lowest level at 15,75 marks. They then hardened again with a brisker business, and to-day again stand at 17 marks.

The prospects of the coming harvest are not favourable, and it is believed that fairly high prices are to be expected.

Orange Oil, sweet. Business in this article has been exceptionally slow and quiet during the past six months, and it is only due to this that the prices have not advanced further, and in fact have even suffered temporarily a slight decline. Although the existing stocks of orange oil were, as early as April, estimated at only about 5000 kilos, and it was thought that this small quantity would quickly be sold, it has taken fully four months to clear it out. In agreement therewith the prices have remained without great fluctuations, and have on the whole kept at the level of 18 marks which had been reached already in April. At the present moment the old stocks are probably completely exhausted.

The prospects of the new harvest were originally very favourable, but in July they commenced to become less and less so, owing to the very large quantity of young fruit dropping off the trees, and at the present moment the new crop both in the Sicilian and the Calabrian producing districts is estimated as barely a medium harvest.

The prices of the new oil will probably remain fairly high, as here in the interior no stock at all, and abroad in any case only small stocks of orange oil are in hand, and for this reason a brisk demand is to be expected. Further, it will be necessary to take more and more into consideration that the constantly increasing despatch of oranges in truckloads to Upper Italy withdraws every year a larger quantity of fruit from the manufacture of essence. As, moreover, contrary to other years, very little business in new oil for forward delivery has been done locally, the prices of new oil will presumably at first come to about 16 marks. The prices may then fluctuate according to the yield of oil of the individual fruit; up to the present the fruit is little developed, owing to the prolonged drought.

Since the foregoing report was written, the condition of the Sicilian and Calabrian oils has scarcely changed, except sweet orange oil, the yield of which so far does not seem to answer the expectations. Under these circumstances the above-cited price of ℳ 16.— is likely to be exceeded during the campaign which has just set in.

According to the results of detailed examinations made by us in the last few years with numerous authentic orange oils, we have now

fixed the following values for orange oil, in the place of those given by us in Gildemeister and Hoffmann's work "The Volatile Oils":

Bitter orange oil: d_{15° 0,854 to 0,857; α_{D20° $+90^\circ$ to $+93^\circ$; α_D of the first 10 % of the distillate higher than α_D of the original oil. Residue on evaporation 3 to 5 %.

Sweet orange oil: d_{15° 0,848 to 0,853; α_{D20° $+95^\circ$ to $+98^\circ$; α_D of the first 10 % of the distillate, not, or but little lower than α_D of the original oil; residue on evaporation 2 to 4 %.

The altered behaviour of the oil as compared with formerly is possibly due to the fact that the selection of the fruit and the expression of the oil used to take place with less care than at present.

Eucalyptus Oil. Nothing new can be reported on this subject. Whilst Algeria comes now but little under consideration as a producing country of fine oil of the Globulus species, Australia supplies abundant quantities, which, however, are rapidly absorbed by the eucalyptol manufacturers. The supply of oils containing phellandrene has also been sufficient; more particularly, there appears to be no lack of oil of *Eucalyptus amygdalina*, which, in view of its low price, plays an important part in the manufacture of cheap soaps.

In his work on the useful plants of the Congo State, E. de Wildeman[1]) also gives a monograph of the eucalypts and the useful purposes to which they are applied, and we add to our numerous notes on this species of plants as follows: Thanks to the far-reaching investigations of Baron F. v. Müller in Melbourne, the eucalypts have been introduced in almost every part of the world. In Europe, the first specimens appeared in the Botanical Garden of Naples at the commencement of the 19th century, but the importance of the eucalyptus as a forest-tree was not recognised in Italy until towards the end of the sixties of last century. In France, the eucalypts were introduced in 1854, and the cultivation was gradually transferred from the Mediterranean regions to the frontier districts. At the same time the French introduced the tree, and especially *E. Globulus*, into their North African colonies, where at present very large plantations are in existence. Since 1870 the cultivation of *E. rostrata* Schlecht. is carried on intensely; the other species are found more in private garden plantations, and are of only limited importance for the cultivation on a large scale. In India the cultivation was commenced in 1863, and the best results there are found in the Nilghiris. At the present time Australia, India, Algeria, and some Mediterranean countries are the

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[1]) E. de Wildeman, Notices sur les plantes utiles ou intéressantes de la Flore du Congo. **1903**, I. 175—221.

principal producers; in North America, where the eucalyptus arrived immediately after its introduction in France, it also gives rise to great expectations. Finally the British Colonies in South Africa come under consideration, but the British and German Colonies in tropical Africa, and the Congo Free State, also carry on the cultivation of eucalyptus successfully. On the lower Congo and in Katanga *E. Globulus* has been selected, in German East Africa and German South West Africa experiments are made with four eucalyptus species: *E. loxophleba* Benth., *E. redunca* Schau., *E. salmonophloia* F. v. M., and *E. salubris* F. v. M.

Next to the palms, the eucalypts are no doubt the most useful trees on earth; they afford shadow and protect plantations against wind; they yield gum, resin, honey, serve as timber for building, as firewood, and for the production of oil. Owing to their rapid growth, all these advantages can be obtained in a comparatively short time. In recent times, india-rubber has been detected in some species, even in the leaves. The eucalypts are also cultivated for mountain forests, but for such purposes the slower-growing species are employed, as they are more resisting and thrive splendidly even at altitudes of 6000 feet. *E. corynocalix* F. v. M., *E. crebra* F. v. M., *E. diversicolor* F. v. M., *E. sideroxylon* Cunn., *E. Globulus* Labill., and *E. tereticornis* Sm. are suitable for this purpose.

It is well known[1]) that *Eucalyptus Staigeriana* F. v. M. growing in Northern Queensland contains an oil with a pleasant and intense odour of lemons and verbena. In their work *"Research on the Eucalypts and their Essential Oils"*[2]) R. T. Baker and H. G. Smith had not described this species owing to lack of material for examination; they now make up for this in a communication in the Pharmaceutical Journal[3]). *Eucalyptus Staigeriana* or *"the lemon-scented ironbark"*, is a small tree with a dark and irregularly fissured bark, and brownish grey leaves which have a lancet-shaped form, are 3″ to 5″ long, and provided with numerous oil cells. The blossoms have an umbelliform arrangement, the fruit is turbiniform, but well-grown. The crude oil was insoluble in 6 vol. 80 per cent. alcohol, and even with 8 vol. it showed still a slight turbidity; α_D —41,1°; d_{16° 0,8708; n_D 1,4871. Below 175° (corr.) only a few drops passed over, at 175 to 193°, 65%. This fraction had the following constants: $d\frac{23^\circ}{15^\circ}$ 0,851; n_D 1,4798. Between 193 and 265°, 23% passed over (d_{23° 0,8828; n_D 1,4846). Between 265 and 300° only traces passed over (n_D 1,5033), and the distillate was quite acid. The various distillates were now rectified, and from

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[1]) Bericht April **1888**, 20; comp. also Gildemeister and Hoffmann, The Volatile Oils, p. 538.

[2]) Reports October **1903**, 38; October **1904**, 31.

[3]) Pharmaceutical Journal **76** (1906), 571.

the fraction between 175 to 193° the limonene tetrabromide (m. p. 104 to 105°) was prepared. From the physical properties the conclusion could be drawn that almost the whole of the terpene consisted of l-limonene. The aldehyde-content of the oil was 15,33 %; the non-aldehydic portion of the oil was very aromatic, and with this portion the ester determination was carried out, which, calculated for the original oil, gave 8,6% ester-content. The geraniol-content was 12,72 %. Bąker and Smith accordingly give the oil of *E. Staigeriana* the following composition: limonene 60,0%, geraniol 12,72 %, geranyl acetate 8,32 %, citral 16 %, indeterminable substances 2,96 %.

L. P. Phillips[1]) uses eucalyptus oil[2]) with chloroform as a vermifuge. The dose consists of 2,5 g. eucalyptus oil, 3,5 g. chloroform, 40 g. castor oil, which an adult takes in two portions. If depression occurs already after the first half, the second half is not taken. Feeble anæmic persons and children are given proportionally less. If necessary the dose has to be repeated every other day until the result is obtained. The treatment was successful in 44 cases, and has this advantage over the use of thymol, that it does not cause depression of the heart.

The therapeutic value of the two classes of eucalyptus oils, cineol oils and phellandrene oils, is up to the present but little known. The British Pharmacopœia prefers that class of oils which is represented by *E. Globulus.* Up to 1898 the oil of *E. amygdalina* was still represented in the British Pharmacopœia. A case of poisoning due to the administration of too large a dose induced F. A. U. Smith[3]) to ascertain whether the oil which had this injurious effect, contained cineol or phellandrene. The faint yellow oil had the specific gravity 0,919 (15,5°), $\alpha_D + 4{,}47°$, and when phosphoric acid (d 1,75) was added formed a semi-solid mass with a red colour. 10 g. of the oil yielded 8,62 g. cineol phosphate, corresponding to 52,6 % cineol. The attempt to detect phellandrene with glacial acetic acid and sodium nitrite gave negative results. In the case in question, 6 fluid drachms (say 18 to 20 g.) of oil had been used, which quantity was sufficient to cause death.

A second case of poisoning with eucalyptus oil is the following: A child aged 2 years 9 months[4]) fell ill owing to having taken

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[1]) Acc. to Zeitschr. d. allg. österr. Apoth.-Ver. **44** (1906), 177.
[2]) Nothing is said as to the species, therefore Globulus oil is no doubt meant.
[3]) Pharmaceutical Journal **76** (1906), 662.
[4]) Brit. Med. Journ. of May 12, 1906. Accord. to Pharmaceutical Journal **76** (1906), 651.

2 fluid drachms of the eucalyptus oil. 15 minutes after taking it, unconsciousness and collapse occurred with contraction of the pupils and stertorous breathing. After administering 10 grains (= 0,65 g.) zinc sulphate, a little whisky and strong coffee, the pupils expanded again, and shortly afterwards consciousness also returned.

Fennel Oil. The harvest in Galicia and the adjoining Russian districts has had a very rich result, and the quality of the new fennel also leaves nothing to be desired from any point of view. For this reason, cheap prices of fennel oil may be reckoned upon this season. It is well known that we distil very large parcels, and supply an oil which owing to its high anethol-content answers the highest requirements with regard to aroma.

Geranium Oils. As we expected, the Syndicate has not succeeded in raising the price of Réunion oil; this may chiefly be due to the fact that no arrangement could be come to, to restrict the production in a suitable manner. We mentioned already in our last Report that an improvement in the situation could only be thought of, if the enormous speculative stocks in Europe were reduced to some extent. Instead of keeping this end in view, it appears that the manufacture has gone quietly on, without considering that a catastrophe would thereby only be accelerated. The stock of oil in Réunion is said to amount to about 15000 kilos, a quantity which, in face of the large shipments of last year (38334 kilos) and the quantities already exported in 1906, must naturally have a very depressing effect on the market. The demand has been greatly overestimated, and it has not been taken into consideration that a large proportion of the production of the last few years has not yet passed over into the consumers' hands, but has been bought by speculators for their purposes.

The export from Réunion this year was as follows: —

January	2779	litres
February	2365	„
March	2257	„
April	5130	„
May	3435	„
June	1062	„
July	1261	„
Total	18289	litres,

as compared with 32192 litres in the same period of 1905. The great falling-off may possibly be attributed to the fact that speculators in the consuming countries have lost faith in this article, and show less inclination to buy.

In April the report spread that a disease (*maladie cryptogamique*) had broken out among the plants in the principal producing districts but this has not been confirmed by the information since received. Lately snow-storms are said to have greatly injured the plantations. But we are too much used to such sensational reports (which generally vanish away into nothing), as to believe in any serious results, the more so, as the distillation is carried on without interruption throughout the year, and as possible damage resulting from natural phenomena is usually quickly remedied by the fertile tropic climate.

Stimulated by the falling exchange in Réunion, the article has lately recovered from the sluggishness which had prevailed for such a long time, being now quoted at Marseilles about 25 fr. per kilo. We fear, however, that the stocks in Réunion are still too heavy to allow of a continued bettering of the market.

The position of Algerian geranium oil is precisely the same, for the production of this article is also out of proportion to the consumption. Locally the price paid at present is 24 francs, and at this quotation almost any quantity desired may be bought. The producers suffer less from the cheap prices than a large number of middlemen, who 1 or 2 years ago were tempted to make large contracts for deliveries over 3 or 4 years, at the quotation of 30 francs which at that time appeared to be low. We are informed that such contracts in one or two cases still run into next year, and the producers who are parties to them are therefore well able to dispose at a cheap price of the surplus quantity of their distillate available beyond the contracts.

According to the *Bulletin de l'Office du Gouvernement général de l'Algérie,* the export of geranium oil in the last three years was

			Average price per kilo
in 1903	to 31 200 kilos	value 1 123 000 francs	36 francs
„ 1904	„ 63 600 „	„ 2 163 000 „	34 „
„ 1905	„ 52 600 „	„ 1 786 000 „	34 „

and in the months of January to the end of July of the present year, 34 600 kilos, value 1 038 000 fr., average value per kilo 30 francs.

We are unable to say how the organ in question proceeds to ascertain the average values; but as the highest price paid this year was 27 francs, and as long ago as the end of January the oil was sold at the present market prices, it may be assumed that this year again, as already mentioned, large parcels have still been shipped at the previous higher contract prices, and in this way the average price could come to as much as 30 francs.

An essential factor in the backward movement of the two geranium oils lies also in the fact that palmarosa oil could, as before, be

obtained in large quantities, although the heavy demand had gradually driven up the prices from 3/6 at the commencement of the season last winter to 5/- and 5/3. The prospects of the new distilling season are this year again not unfavourable, so that it may be assumed that the first offers of new oil at 5/- will soon be followed by lower quotations. Before this new oil is available several months will still pass, and during that time, in view of the reduced stocks, cheaper quotations than the present ones can hardly be expected.

Gingergrass oil was almost entirely absent during the last few months. This oil is now quoted in London at 5/6, and consequently is dearer than palmarosa oil.

The last time we published the results of our examination of gingergrass oil[1]) we stated that we had not yet succeeded in identifying dihydrocuminic alcohol by a solid derivative. Now, we recently found in α-naphthyl isocyanate a reagent, which, similar to phenyl isocyanate, forms with alcohols naphthyl urethanes, and which in the present case reacts with dihydrocuminic alcohol, with formation of a solid derivative. The reagent in question has not yet been used for the characterization of alcohols, and we believe that we are justified in recommending its use with those bodies in all cases where non-crystallising urethanes are obtained with phenyl isocyanate. Unfortunately, the naphthyl urethanes appear to have the disagreeable property of a very difficult combustion in the elementary analysis. At least we have in the analyses of all the following derivatives obtained carbon values which differed up to 3 % from those required in theory. On the other hand, the hydrogen figures generally agreed well with those calculated theoretically. With the exception of one analysis of the geraniol derivative, we have always obtained negative results, in spite of numerous repetitions.

Geranyl naphthyl urethane. A mixture of equimolecular quantities geraniol and α-naphthyl isocyanate heats fairly rapidly, and congeals into a solid mass already in 12 hours. For purification, dilute methyl alcohol is most suitable. Long needles, m. p. 47 to 48°.

0,1710 g. subst.: 0,4871 g. CO_2, 0,1281 g. H_2O.

	Found:	Calculated for $C_{21}H_{25}NO_2$:
C	77,68 %	78,02 %
H	8,32 %	8,74 %

Dihydrocuminyl naphthyl urethane. The crude product which solidified after 24 hours, is a mixture of two naphthyl urethanes, from which one, the more difficultly soluble, can be isolated by fractional crystallisation by means of methyl alcohol. Brilliant prisms of the

[1]) Journ. f. prakt. Chem. II. **71** (1905), 459; Report April **1905**, 41.

m. p. 146 to 147°. The other more readily soluble derivative may possibly melt below 100°, and be identical with geranyl naphthyl urethane.

Terpinyl naphthyl urethane from terpineol of the m. p. 35°. The reaction-mixture does not become solid even after standing for 6 days. The oily product is treated with water vapour, and the solid distillation-residue boiled out with petroleum ether. From dilute alcohol the urethane crystallises in feathery prisms of the m. p. 147 to 148°. The derivative of terpineol of the m. p. 32° is also purified from alcohol. Hard, glassy prisms of the m. p. 83 to 84°.

Linalyl naphthyl urethane. For the production of this derivative it is necessary to heat for several hours the mixture of linalool and naphthyl isocyanate, after it has been standing for 5 to 6 days; but even then only very little has been formed. The urethane crystallises from dilute methyl alcohol in rosette-shaped needles of the m. p. 53°.

From nerol and citronellol, only oily naphthyl urethanes were obtained which did not crystallise even when cooled and when left standing for weeks.

Heracleum Oil. It is now well known that this oil is obtained from the fruit or the entire umbellate heads of *Heracleum sphondylium* L. A distillate which we have obtained from the dry umbels from which the fruit had been removed, is for this reason interesting. The yield of oil amounted to 0,08 %. The odour of the brownish yellow oil differs distinctly from that of the fruit. d_{15° 0,9273; α_D — 0° 48′; acid no. 16,2; ester no. 148,6; ester no. after acetylation 195,9; soluble in 1,1 vol. 80 per cent. alcohol; when more solvent is added opalescence and strong separation of paraffin occur. For comparison we give below the properties of two oils distilled from the fruit only.

1. Yield (compared with dry material) 0,9 %; d_{15° 0,8744; α_D + 0° 38′; acid no. 15,9; ester no. 215,4; ester no. after acetylation 285,3; soluble in 0,8 and more vol. 80 per cent. alcohol; not entirely soluble in 70 per cent. alcohol.

2. Yield (compared with dry material) 1,21 %; d_{15° 0,8798, α_D + 1° 6′; acid no. 7,3; ester no. 242,4; ester no. after acetylation 276,3; soluble in 1 and more vol. 80 per cent. alcohol.

A distillate from the dry, ripe fruit of *Heracleum giganteum* L. (yield 3,6 %) behaved as follows: d_{15° 0,8722; α_D + 1° 14′; acid no. 1,6; ester no. 288,3; ester no. after acetylation 314,2; soluble in 1 and more vol. 80 per cent. alcohol. The colourless oil had a peculiar odour, similar to that of common heracleum oil.

Hop Oil. We are informed that the development of the hop plants has been retarded by unfavourable weather, and that in many districts the gardens have suffered much from the spread of pests.

Only with the commencement of better weather early in August, the condition of the plants improved, at least as far as the undamaged plantations are concerned. As the ripening and picking will take place this year about a fortnight later than last year, the reports received up to the present are largely contradictory, and do not enable one to form a clear opinion on the probable results of the harvest.

At the present moment, this year's results, as compared with those of 1905, are estimated as follows: in Bavaria partly at 1/5, partly at 3/4 to 7/8, on the average at a feeble 3/4; in the other German countries and in Austria-Hungary at a bare 2/3, in England and Russia at scarcely 1/2, in Belgium at 1/3, in France at 3/4 of last year's crop, whilst North America hopes to show equally favourable results as in 1905.

In spite of the unfavourable prospect, the prices of hop will not advance to an extraordinary height, as all interested parties have covered themselves last year for a long time to come at the advantageous prices, and during this season a proportionately smaller demand will probably be made on the market.

Our prices of hop oil of our own distillation remain for the present unchanged.

Lavender Oil. Owing to the exceptional drought which prevailed during the spring and summer months in the South of France, the results of this year's distillation have fallen far below the expectations, and the regrettable fact must be stated that only one half of the result of a medium harvest can be reckoned upon. Dealing with the individual producing-districts, our informant reports that those in the departments Basses- and Hautes-Alpes, which are situated at the greatest elevation, have suffered least owing to occasional showers, and that in a few places the results are said to be almost normal. On the average, the results in these departments may be called 2/3 of the normal. But in the Alpes-Maritimes, in Var and Drôme, the crop is only equal to one half, whilst the department Vaucluse has suffered most from the unfavourable weather-conditions, so that hardly more than 1/4 or at most 1/3 of an average harvest has been obtained.

In view of these facts it is not surprising that at the two first markets at Digne and Sault, new distillate fetched prices considerably higher than those of last year, although, as is well known, last year's prices were not the normal ones corresponding to the rich yield of the harvest, but had experienced an unnatural rise owing to the speculative driving up of the prices by certain firms. As matters stand at present, the prices will doubtless not remain at the level of those paid at present, varying on the spot from 28 to 35 fr. per kilo, according to quality, as the production does probably not by a long way meet the requirements of the consumers.

Our factory at Barrême, situated in a neighbourhood where, as mentioned above, the conditions were of the most favourable, has supplied an amount about equal to that of 1905, so that we are unfortunately, even after the end of this season, still unable to place any quantity worth mentioning on the market. The approximate quantity of 1500 kilos at our disposal, which this year again shows an average ester-content of 52 %, has to be reserved for a few clients who have secured this quality in advance "à tout prix" for special purposes. By means of definite agreements with the principal parties interested in the blossom-industry, we had succeeded in keeping the prices of the distillation-material within reasonable limits, so as to prevent from the first the spread of unauthorised rumours like last year.

We need not remind our readers that a large number of envious competitors in the South of France had accused us of forcing up the prices in our purchases of blossoms and oil, and of being the cause of the high prices of last season. It is all the more ridiculous that this year the opposite tactics are followed, and it is attempted to make us unpopular with the producers by accusing us of price-cutting! A local paper in the South of France, on the occasion of a report on the market at Digne, expresses the hope that these profitable prices will remain in force, so that all small producers may be able to hold their own against the 'Compagnie Schimmel d'Allemagne', who would have liked nothing better than that the prices had not been above 20 francs. We would not withhold this little jest from our readers, in order to prove that it is unfortunately an impossibility to meet the wishes of everyone over there.

With reference to what we said in our last Report, we wish to state that Mr. Lautier Fils of Grasse, the firm who expressed doubt that there existed a natural oil with such a high ester-content as what we obtained, has taken samples at our Barrême factory during the last distillation. In the meantime we have received a communication that he had convinced himself of the truth of our statement regarding the ester-content of our product. This disposes of the matter as far as we are concerned.

In a work on the influence which the cross-fertilisation of lavender and spike has on the essential oil of these plants, A. Birckenstock[1]) also deals with the ester-question. Although he places himself on the standpoint likewise occupied by us, that the ester-content is highly important for the valuation of lavender oil, and that the classification of the various qualities according to their content of linalyl acetate

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[1]) A. Birckenstock, Action de l'hybridation sur les essences de lavar[illegible] aspic. Moniteur scientifique de Quesneville, May 1906.

as a rule applies, he has observed that there are also good lavender oils which contain only 20 to 30% ester.[1]) Such oils are found in the Alps near the Franco-Italian frontier, and the annual production (about 5000 kilos) is in Birckenstock's opinion of sufficient importance to take the particular properties of these oils into account. They have a very fine bouquet, but no "body". The content of linalool amounts to about 50%, and is therefore normal, but, as already mentioned, the ester-content is only 20 to 30%; they are also characterised by a low specific gravity (0,878 to 0,882), and by a considerable lævo-rotation (— 8 to — 9°); they are, moreover, very readily soluble in alcohol (in 10 to 12 vol. 60 per cent. alcohol).

A further exception to the rule, according to Birckenstock, is made by the varieties standing between lavender and spike. If, namely, lavender comes below 2300 to 2600 feet, it crosses with spike, "elle s'aspique"; the hybrids thus formed are known among distillers by the names of *"lavandin"* or *"spigoure"*, and they represent every possible transition between lavender and spike, according to the conditions due to altitude and state of the soil. In this connection Birckenstock's statements on the morphological differences between lavender and spike are also interesting; lavender has a non-ramified stalk, which is rarely longer than 16 inches; the blossoms are blue-violet, and have thin, heart-shaped, pointed sepals which are shorter than the bluish calyx.

The spike plant is larger than the lavender. The stalks frequently have several ramifications, and grow to a height of up to 32 and 36 inches. The sepals are linear and of the same length as the calyx, which in this case is not bluish, but whitish.

The influence of cross-fertilisation also shows itself in the properties of the essential oils, which behave entirely like mixtures of lavender oil and spike oil. Birckenstock has in the course of his observations examined a whole series of oils, from typical lavender oil to typical spike oil. He then found at the same time that towards lavender oil not only the ester-content and alcohol-content increase, but that also a gradual change takes place in the proportion of borneol to linalool and geraniol; whereas in spike oil borneol predominates, it diminishes towards lavender oil more and more as compared with linalool and geraniol. We give here still the properties of two characteristic lavandin oils:

1. d_{15° 0,9027; α_D — 0° 43′; ester-content 6,23%; alcohol-content ($C_{10}H_{18}O$) 34,8%; soluble in 3 vol. 65 per cent. alcohol.

2. d_{15° 0,8995; α_D — 1° 35′; ester-content 9,12%; alcohol-content 36,5%; soluble in 3 vol. 65 per cent. alcohol.

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[1]) Comp. Report October **1904**, 51.

We have here briefly reproduced Birckenstock's statements, owing to the special interest which this subject, hitherto not mentioned by us, possesses. Yet lavandin oil does not form an exception to the ester-theory, formulated for lavender oil, as it is no longer the oil of the actual lavender-plant, but of a hybrid, and (as Birckenstock justly remarks) it is a matter of no concern to the trade whether it is a question of a lavender oil adulterated with spike oil, or of an oil which may be pure, but yet behaves exactly like the above-named mixture.

Lemongrass Oil. As already predicted in our April Report, a reaction has at last come in the price of this article, and the market has dropped from $8^1/_2$ d. per oz. in April to 3 d. per oz. It is to be hoped that the remunerative prices of last year have not induced the planters to extend their plantations too much, for in such case they would undoubtedly suffer a very severe disappointment. Although the oil of *Backhousia citriodora*, with an aldehyde-content of about 98 %, consisting chiefly of citral, has not yet been shipped in large parcels, it can (as we hear from an absolutely reliable source) be supplied in such quantities, and in spite of the high wages in Australia, in case of need at such a low price, that lemongrass oil, even at a price of 3 d. to 4 d. per oz., can no longer come under consideration for the manufacture of citral. We think it well, however, to point out to the Australian optimists that the citral manufacture is by no means exclusively dependent upon lemongrass oil and Backhousia oil, but that other cheap raw material has also to be taken into account.

The shipments from Cochin during last season, i. e. from 1st July 1905 to 30th June 1906, amounted to: —

	$190^1/_2$	cases to	London
	100	„ „	Havre
	200	„ „	Marseilles
	$218^1/_8$	„ „	Hamburg
	$330^1/_2$	„ „	New York
	$1230^1/_{12}$	„ „	Asiatic ports (Bombay and possibly subsequently Europe).
Total	$2269^5/_{12}$	cases.	

For the sake of comparison, we quote here again the shipments of the last few years: —

1904—1905	$1881^1/_2$	cases
1903—1904	$2222^1/_2$	„
1902—1903	2806	„

Through the kindness of Mr. P. Bussy we received a sample of lemongrass oil which had been distilled in the Government laboratory at Saigon (Cochin China). It had the following properties: d_{15° 0,8917;

α_D — 0° 10′; aldehyde-content about 82%; insoluble in 10 vol. 70 per cent. alcohol; soluble in 0,9 vol. 80 per cent. alcohol, when more solvent is added soon strong turbidity; with 90 per cent. alcohol it forms at first a clear solution, but when more than 1,5 vol. are added, cloudiness occurs. According to these results the oil behaves like the West Indian and African lemongrass oils, which we have repeatedly referred to in our Reports[1]). Owing to the deficient solubility, the oil has a lower commercial value than the ordinary East Indian lemongrass oil.

Oil of Leptospermum Liversidgei. Several years ago we reported already on the oil of a species of *Leptospermum*, viz., *Leptospermum scoparium,* according to researches by C. E. Atkinson[2]). We have now before us a work by R. T. Baker and H. G. Smith[3]) on the oil of *Leptospermum Liversidgei* (called after A. Liversidge, Professor at the Sydney University). The crude oil was insoluble in 10 vol. 70 per cent. alcohol, soluble in 1 vol. of 80 per cent.: $d_{15°}$ 0,8895; $\alpha_D + 9{,}2°$; $n_{D16°}$ 1,4493. At 170° 20% of the oil distilled ($d_{15°}$ 0,8624; $\alpha_D + 32{,}5°$; $n_{D16°}$ 1,4774), between 195 and 225° 30% ($d_{15°}$ 0,8892; $\alpha_D + 5{,}7°$; $n_{D16°}$ 1,4892). The principal constituents of the oil are citral (35,0%; naphthocinchoninic acid, m. p. 199°), recognisable by its characteristic odour; further, geraniol (9,74%), slightly covered by the odour of citral; geranyl acetate (5,35%), and d-pinene (25%; nitrosochloride, m. p. 103°), and finally, in addition to one which could not be determined, a sesquiterpene (24,91%; $d_{15°}$ 0,9024; $n_{D16°}$ 1,5052). Limonene and phellandrene were not detected.

Linaloe Oil. The value of this important perfume has since the spring gradually risen to 17 marks per kilo, and the Hamburg importers, who have practically monopolised now for some considerable time the trade in this article, appear little inclined to concessions, although there are numerous indications that the European market has laid in an abundant supply in good time. Cheaper offers from second-hand are not rare. The report recently spread, that several factories for the rational distillation of linaloe oil had been established in Mexico, does not appear to find confirmation; on the contrary, it is said that the production is still carried on by Indians by means of portable and very primitive apparatus. We are informed that the firmer tendency of the market during the last few months is not at all due to lack of oil, but must be attributed simply to successful operations of the Mexican exporters.

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[1]) Comp. Report April **1906**, 44; also October **1902**, 50; April **1903**, 23, 49; October **1903**, 46; October **1904**, 53; April **1905**, 84.

[2]) Report April **1903**, 50. Accord. to Pharmaceutical Journal **69** (1902), 369.

[3] Accord. to a reprint from the Journ. and Proc. of the Royal Soc. of N. S. Wales, **1906**.

The observations which we have already repeatedly made previously[1]) that there are also dextrorotatory linaloe oils of otherwise good quality, has recently been confirmed from various sides. For example, E. J. Parry and C. T. Bennett[2]) have observed in two oils a dextrorotation of $+2^\circ 30'$ and $+4^\circ$, whilst those determined by us were $+2^\circ 54'$, $+6^\circ 3'$, $+7^\circ 31'$, and even $+8^\circ$. We also at the time called attention to the fact that the d-linalool isolated by us from the dextrorotatory oils, had been included in our lists. We therefore need only refer to the above statements. Parry and Bennett[3]) further found in oils from a reliable source, an extraordinary high ester-content (11,2 %) with a corresponding low linalool-content (57 %); in this case the rotation was -13°. Apart from the fact that we also had found similar results in oils which otherwise were unobjectionable, H. Simmons[4]) also confirms this as well as the former statements. He found on the one hand in an oil a rotation of $+5^\circ 14'$, and on the other hand ester-contents of 6,29 to 9,0 %. Yet W. Naumann[5]), who also quotes some results of analyses of linaloe oils, has up to the present never observed a dextrorotation of these oils. An explanation of the striking occurrence of dextrorotation is possibly given by A. Birckenstock, whose work on rue oil, rosemary oil, and lavender oil is quoted in these Reports[6]).

Oil of Myrrh. With reference to a work by A. Tschirch and W. Bergmann[7]) on Herabol myrrh, E. M. Holmes[8]) expresses himself somewhat as follows: The statement made by Tschirch, that Holmes, while rejecting all the other mother-plants, wishes only to admit *Commiphora myrrha* (Nees) Engl. (*Balsamea myrrha* Baill.), but not also *Balsamodendron myrrha* Nees, as crude material for the production of this drug, does not agree with the facts. Holmes refers to an earlier work[9]) in which he mentions exactly *Balsamodendron myrrha* Nees as the mother-plant of the drug. Holmes also denies Tschirch's assertion, that Holmes' objections to Schweinfurth's[10]) statements are based solely on the determination of the odour and taste.

Neroli Oil. The rumours already mentioned in our last Report, according to which one half of the orange-blossoms had been destroyed

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1) Report April **1904**, 56; October **1905**, 47.
2) Chemist and Druggist **68** (1906), 544.
3) loc. cit.
4) Ibidem, 584.
5) Ibidem, 619.
6) Comp. the present Report under the respective headings.
7) Arch. der Pharm. **243** (1905), 641; Report April **1906**, 46.
8) Pharmaceutical Journal **76** (1906), 254.
9) Ibidem **62** (1899), 27.
10) Berichte d. deutsch. pharm. Ges. **3** (1893), 237.

by the severe frosts in March, have unfortunately been confirmed, and as a consequence the prices of the blossoms rose in a short time to 2 francs per kilo. As but little oil was available from last year, the price of neroli oil advanced up to 1000 francs per kilo. It is not surprising that but few purchasers are willing to pay such a price, the less so as our artificial neroli oil offers to the perfumery trade a substitute, than which a more serviceable is inconceivable. The demand for the latter was consequently exceptionally brisk, and we have every reason to believe that a large number of doubters have this year, driven by necessity, convinced themselves that our artificial neroli oil possesses as a matter of fact the advantages ascribed to it, and that it must be recognised as a substitute fully equal to the genuine distillate.

We abstract from the "Petite Revue agricole et horticole" the following details on the financial prospects of the cultivation of orange blossoms: The expenses of the establishment of orange-gardens are very high, and are estimated at at least 3000 francs per hectare (say £ 50 per acre). Not until after ten years do the plantations give half a usual crop, and a full one only after twenty years. There can be no question of profit, unless after 20 years the annual net result of 4000 francs per hectare can be reckoned upon, corresponding to a selling price of the blossoms of 0,60 francs per kilo. This, as is well known, is the minimum price, which the "Société coopérative des propriétaires de fleurs d'oranger" has held out as a prospect to its members, as the result of its efforts[1]).

Oil of Cretian Origanum. We recently detected cedar camphor in a Smyrna origanum oil from *Origanum smyrnaeum* L. The oil had the following physical properties: d_{15° 0,9386; phenol-content 41%, soluble in 2 to 2,5 vol. 70 per cent. alcohol. The sesquiterpene alcohol crystallised out from the highest-boiling portions which in the distillation with water vapour pass over as a milky distillate. The quantity may possibly amount to 5% of the original oil. After pressing out and sucking off the adhering oil and recrystallising from dilute alcohol the substance formed needle-shaped crystals (m. p. 81 to 84°), which when further recrystallised from petroleum ether melted somewhat constant at 85,5 to 87°; $[\alpha]_D + 8^\circ 48'$ (in 10% chloroform solution). The values determined by elementary analysis pointed to an alcohol of the formula $C_{15}H_{26}O$: —

0,1694 g. subst.: 0,4985 g. CO_2, 0,1820 g H_2O.

	Found	Calculated for $C_{15}H_{26}O$
C	80,73%	81,08%
H	12,00%	11,71%.

[1]) Report October **1904**, 60.

A depression of the melting point of a mixture of the foregoing sesquiterpene alcohol and cedar camphor was not observed. From these results it could already be concluded that the two bodies were identical. A further proof in support of this was the identical behaviour of the two substances towards phenyl isocyanate. In both cases a phenyl urethane of the m. p. 106 to 107° was obtained, although only when the reagent was heated to its boiling point. Our previous[1]) statement that cedar camphor does not form a phenyl urethane with phenyl isocyanate is therefore incorrect. The derivative crystallises very well from dilute alcohol in brilliant prisms of the above melting point.

Elementary analysis of the phenyl urethane: —

0,1529 g. subst.: 0,4315 g. CO_2, 0,1299 g. H_2O.

	Found	Calculated for $C_{22}H_{31}NO_2$
C	76,97 %	77,42 %
H	9,44 %	9,09 %

Towards strong formic acid the sesquiterpene alcohol also behaved exactly as cedrol. The hydrocarbon thereby formed corresponded in its physical properties entirely with cedrene. After distillation over sodium, the following was found for it: b. p. 260 to 261° (752 mm. pressure); α_D — 95° 46′; $d_{15°}$ 0,9368; $n_{D20°}$ 1,49807. Whether cedrol is a normal constituent of Smyrna origanum oil, or whether it has been introduced by adulteration with cedar oil, is a question which we cannot answer. The latter is not exactly improbable, as Smyrna origanum oil, as we were recently able to detect, is adulterated in the coarsest manner.

From the "Pharmazeutische Zeitung"[2]) we abstract the following paragraph with reference to the physiological action of oil of Cretian origanum: A man who used *Oleum origani cretici* (1 + 2 *spir. vini*) as a remedy against toothache, and carelessly swallowed the oil, was attacked on two succeeding days by tetanus which lasted 6 hours each time. According to experiments made by Kobert[3]) jointly with B. Küssner, carvacrol, the principal constituent of the oil, when administered to man in medicinal doses, has no injurious effect, apart from local symptoms of irritation of the mucous membranes. Yet Bälz[3]) observed already after small doses, in some individuals, buzzing in the ear, headache, severe delirium and even collapse with symptoms of paralysis, and somnolence. Large doses administered to animals have a paralysing action without previous central

[1]) Report October **1904**, 24.
[2]) Pharm. Ztg. **51** (1906), 481.
[3]) Kobert, Lehrbuch der Intoxikationen, 1904, Vol. II, p. 132.

irritation. The case mentioned above might possibly also be attributed to the injurious effect of carvacrol. According to another communication[1]) no such case has been observed during 20 years' administration of the oil in undiluted condition.

Orris Oil. In continuation of their information on the orris-root market in our April Report, our correspondents describe the present situation as follows: —

What strikes us in the first place in reviewing the past 12 months is the enormous improvement in the prices which has occurred in this period, for whilst in August 1905 assorted roots were quoted 36/37 marks cif. Hamburg, the price in July 1906 was 65 and in some cases even 70 marks. Who would have thought a year ago that such a revolution could take place in so short a time! At that time a Florentine speculator sold important quantities uncovered for delivery over 1906, and there can be no doubt that this must have been a very costly experience to him.

This considerable advance may probably be explained chiefly by the almost uninterrupted demand, and in the respectable export-figures, which have risen from only 500 tons in the period from 1st September 1904 to 31st August 1905, to 920 tons in the succeeding twelve months. It appears to be a fact that the old stocks had been completely used up, especially in France, as the demand from that country was particularly brisk.

At the end of February the available quantity was . .	about 660 tons
If we deduct from this the shipments from the beginning of March to the end of August	„ 370 „
There remain in stock on 1st September 1906	about 290 tons

We repeat here the exports of the last four seasons: —

September 1902/August 1903	about 840 tons
September 1903/August 1904	„ 820 „
September 1904/August 1905	„ 500 „
September 1905/August 1906	„ 920 „

and the avaible total quantities: —

September 1902/August 1903	„ 1400 „
September 1903/August 1904	„ 1310 „
September 1904/August 1905	„ 1160 „
September 1905/August 1906	„ 1210 „
September 1906/August 1907	„ ??

If the present good selling prices continue, everything will doubtless be gathered which is ripe for the harvest; a total quantity which, owing to the continued restriction in the quantities planted out, may possibly not exceed 500, or at most 600 tons. But apart from this, the producers now fall back everywhere upon the old roots which had apparently been forgotten, and which had not been gathered when they were ripe, as the low market quotations at the time did not pay for the gathering expenses.

These roots, which are 4, 5, and even 6 years old, cause a good deal of waste when being trimmed, as they cannot be peeled like 2 or 3 year old roots which are still juicy, but on the contrary the rind has to be cut off with the knife, what naturally causes much loss. Only the tempting selling prices could effect the miracle that these old roots, which for the rest can only be sold as seconds, have been fetched out at all. According to our

[1]) Pharm. Ztg. **51** (1906), 566.

correspondents their total quantity may possibly come to 200 or 250 tons; in such case the total crop would work out at 500 to 600 tons regular and 200 to 250 tons old roots, i. e. 700 to 850 tons in all. With a result of 850 tons, there would be available for the season September 1906/August 1907, including the above-mentioned balance of 290 tons left over from last season, a total of 1140 tons altogether. This would be a good supply as compared with the average annual export, but on the other hand, if everything is now cleared, the 1907 harvest will be all the smaller owing to the reduced quantities planted out during the last few years.

The movement of the prices during the past 12 months was approximately as follows: —

1905	September/October	36/38 marks
	November/December	38/43 „
1906	January/February	43/47 „
	March/April	47/54 „
	May/June	54/62 „
	July	62/70 „
	August	64/67 „

The highest price of 70 marks was only paid in one or two cases at the end of July.

The quality of the new crop leaves something to be desired, the same as in the last few years.

Since a reaction has taken place after the highest point was reached in July, because the buyers abroad disregarded the higher quotations, the article can at present be valued nominally at about 62/64 marks cif. Hamburg for assorted roots, and 55/57 marks for seconds. Fluctuations in the price will of course frequently occur at the present time, during the harvest, according as offers to sell, or the inclination to buy preponderates. Up to the present no transactions of any importance have taken place in the new roots, as so far only small orders for export have been received. People are clearly waiting how the situation shapes itself, but a big drop in the prices seems from the above data to be out of the question.

With regard to the Veronese roots, which of course mature at a later period, our informants report that the crop, according to all calculations, will again be very small, as the cultivation of orris-root has been discarded for other more remunerative cultures, among which principally sugar-beet.

Pastinaca Oil. We have this year distilled pastinaca oil, and that for the first time from cultivated plants (*Pastinaca sativa* L.) from the irrigated fields at Miltitz. We submitted separately to distillation with water vapour, the ripe dried seeds, the umbels, and the roots of the plants.

1. Oil from dry seed of *Pastinaca sativa* L.: The bright yellow oil obtained in a yield of 1,47 % had the following properties: d_{15° 0,8736; α_D — 0° 9′; n_{D20° 1,43007; acid no. 4,4; ester no. 240,6; ester no. after acetylation 276; soluble in 2 ½ and more vol. 80 per cent. alcohol.

2. Oil from dry umbels of *Pastinaca sativa* L.: The oil had a dark-brown colour, and had a very remote odour of oil of ambrette seeds. It was obtained in a yield of 0,3 %; d_{15° 1,0168; α_D — 0° 50′; n_{D20° 1,50049; acid no. 4,2; ester no. 62,9; ester no. after acetyl-

ation 86,2; soluble in 6,5 vol. 80 per cent. alcohol, with separation of paraffin.

3. Oil from the dry roots of *Pastinaca sativa* L.: The bright yellowish oil, which in the odour reminded somewhat of vetiver oil, was obtained in a yield of 0,35 %, and had the following properties: d_{15° 1,0765; α_D — 0° 10′; n_{D20° 1,52502; acid no. 3,9; ester no. 12,6; ester no. after acetylation 33,7; not completely soluble in 10 vol. 80 per cent. alcohol; soluble in 0,6 and more vol. 90 per cent. alcohol.

Patchouli Oil. During the last few months we were able to reduce still further the prices of this article, indispensable for the perfumery trade, but it appears that now a certain stability has been reached, and we do not believe in a further decline. There is little raw material on offer at present. The cheap Indian distillate can of course not compete in quality with our oil, the production of which is one of our particular specialties.

Oil of European Pennyroyal. There is a great scarcity in this oil, as the harvest in Spain is a complete failure. Algeria also supplies very little this year, and it will be necessary to consider the question of adopting a substitute wherever possible. The American oil is at present quoted at $ 2,25 per lb., which is probably too high for most purposes.

Peppermint Oil, American. A report from our New York branch, drawn up on the spot as previously in every year and, in view of the many existing contradictory communications made for special purposes, possessing particular value, describes the situation as follows: —

I. Wayne County, New York.

Owing to the moderate fall of snow and the severe cold during last winter, a large proportion of the peppermint roots was destroyed, and the plants not affected by the frost have grown but sparingly. Although in some districts an increase in the area cultivated with peppermint was at first reported, the total result will fall far short of that of last year, as in several districts, as for example Sodus, Marion, and Palmyra, very little has been newly planted, and the oil-yield is also said to be lower. Whereas in former years the yield from newly planted peppermint amounted to 40 to 60 lbs. per acre, the expectations this year are only 20 to 30 lbs. Older plants produce only 7 to 10 lbs.

In order to allow as much time as possible for the development of the plants, the distillation has been postponed 3 to 4 weeks, and as the weather during that time was favourable, the producers will not regret of having taken this step.

The value of landed property has risen considerably during the last few years, and as the roots are still scarce and dear, it may be assumed with a fair amount of certainty that the peppermint oil industry in Wayne County will not again attain its former dimensions. In some districts complaints are also made about considerable difficulties in procuring labour.

The following area is under cultivation with new plants: —

Williamson	4 acres
Marion	$37^1/_2$ „
Palmyra	$23^1/_2$ „
Sodus	38 „
Arcadia	151 „
Junius	$12^1/_2$ „
Galen	12 „
Rose	$5^1/_2$ „
Lyons	125 „
Phelps	7 „
Total	416 acres.

If the yield of oil is calculated at 25 lbs. per acre, this would give a result of 10,400 lbs. We estimate the plantations of last year's and of older peppermint at about 300 acres, which with a yield of 7 lbs. per acre would produce 2100 lbs. To this should be added the stocks of last year's oil, 5300 lbs., which were held back by the producers in the expectation of higher prices, so that this year in all about 17,800 lbs. Wayne County oil will be available for consumption.

II. Michigan and Indiana.

In Michigan the following area is this year under cultivation with peppermint: —

Berrien Co.	805 acres,	of which newly planted 175
Cass Co.	205 „	„ „ „ „ 25
St. Joseph Co.	1043 „	„ „ „ „ 168
Branch Co.	340 „	„ „ „ „ 40
Kalamazoo Co.	680 „	„ „ „ „ 120
van Buren Co.	1218 „	„ „ „ „ 152
Allegan Co.	2180 „	„ „ „ „ 890
Muskegan Co.	785 „	„ „ „ „ 95
Total	7316 acres.	

The aspect of most fields is not particularly gratifying. In consequence of cold weather during the spring months, the plants are very backward, and at the time when they really ought to be about a foot high, they measured only 4 to 6 inches, whilst the shoots which are so important for the result, were almost entirely absent. Although

the land under cultivation is larger than last year, there is no three-year old peppermint, and that of two years old is in a very bad condition. What was planted out this year has suffered considerably from the continuous frosts during the spring, so that the fields had to be cut back several times. In most districts the damage is estimated at about 50%, and it is believed that not more than about half the 1905 harvest may be expected.

In Indiana the state of affairs is not any more favourable, as about half the new plantations have been destroyed by frost. Altogether 1149 acres are under cultivation in that State, of which 169 acres were laid out this year.

The total result of the American peppermint oil production in 1906 is therefore estimated as follows: —

Wayne County (incl. remainder of 1905)	about	17800	lbs.
Michigan	„	92000	„
Indiana	„	12500	„
Total	about	122300	lbs.

against about 240000 lbs. last year.

This, according to the information collected by our representative, was the position about the end of July, and it is not surprising that on the strength of these particulars the tendency had to be characterised as very firm.

Now we have recently been informed that the oil-yield in Wayne County comes out more favourably than was originally anticipated, and that consequently more oil may be expected from there; in the other districts the situation appears also to have been considered from a too pessimistic point of view, and the belief has recently been expressed than an estimate of a total result of 175000 to 200000 lbs. will more closely agree with the facts. The firm tendency has as a consequence given way to a certain dullness which is also reflected on the European markets.

The producers themselves do not appear to have much faith in remunerative prices, for they have considered it an opportune moment to form an organisation for maintaining the prices, whose purposes are evident from a circular reading as follows: —

"As all classes, except farmers, are organized for protection, we believe all branches of farmers should be, and inasmuch as the organization known as the American Society of Equity proves to be successful, we, Essential Oil Growers organize in this Society and submit the following for your approval.

Name of Society: The American Society of Equity. Essential Oil Department.

We, Essential Oil Growers join ourselves together for the purpose of securing profitable prices for our product, and protection.

That we advise an acreage and crop report from all Mint Growing Districts, by reliable reporters in this society, mode of selection of reporters and kind of report to be determined. Also officers and duties to be designated.

When distilling is done and crop report in, we deem it advisable for a Board of Directors to fix a minimum or lowest price, if possible all get that price.

Some provision to be made for those who cannot hold for the price (minimum).

And as we believe essential oils are adulterated much to the detriment of growers, this should receive the attention of this body. And as we believe these hindrances can only be removed by all branches of farmers holding together as one man.

For this reason it is deemed advisable that all branches of farmers should be organized under one general head, and in one solid body, for equitable prices for all farm products.

We advise also in this case of too great a surplus of oil that the acreage should be diminished and encourage crops instead, thus balancing crops and prices.

That crop reports are the property of members of this society only, and that those who derive benefits from this organization should be members and help bear the expenses.

That we meet in the unions of this Society, but if advisable Mint Growers to have separate meetings for their particular business.

That we adopt for our official paper 'Up-to-date Farming', and give all branches of the Society our hearty support and co-operation.

That we propose a convention of Mint Growers, possibly at the same time of the Potato and Fruit Growers, to formulate the Mint Growers' Branch of the A. S. of E. and elect officers and attend to whatever business may come before the Convention.

Do you favor this or a similar plan? Kindly advise.

(Signed) The American Society of Equity
Geo. C. Wattles, Organizer, Sherwood, Mich."

Although certain interested parties have from the first applied to the Government to take steps against the new Organization as being contrary to the Anti-Trust Law, the first meeting took place on the 5th September at Kalamazoo, and was also attended by our authorised agent as a spectator. The resolution passed on that occasion was as follows: —

"Whereas the principal producers of oil of peppermint have carefully considered the cost of producing the said commodity throughout the entire oil producing belt and have ascertained systematically the available quantity for consumption during the coming year,

And whereas the present high price of labor and unfavorable natural conditions have tended to both reduce the acreage and also largely increase the cost of production,

And whereas there has been considerable agitation among the New York and other buyers regarding the fixing of a minimum price by the growers and primary owners and holders of essential oils,

And whereas there is a feeling among the said growers that the initial price of oil of peppermint should be materially higher than last year,

And whereas it is deemed by competent judges that oil peppermint ought to be placed upon the market at from $ 3,— to $ 4,— per lb. in order that growers may receive a fair compensation for capital and labor invested,

Therefore be it resolved, that we do recommend that the minimum price of oil peppermint in the producing districts throughout this jurisdiction be not less than $ 2,75 to $ 3,— per lb. as per quality,

And further resolved, that even higher prices are justifiable under the circumstances.

Whereas this branch of the American Society of Equity is known and recognized as the essential oil branch,

And whereas at this time nothing has been done or said in regard to any other essential oil produced in marketable quantities in this jurisdiction other than oil peppermint,

And whereas it is not deemed advisable at this time to make recommendations regarding prices or productions of said other essential oils.

Therefore be it resolved that we do not deem it advisable or necessary at this time to take into consideration matters pertaining to the production and marketing of such essential oils other than oil peppermint produced within our jurisdiction, but stand ready to consider all matters of this nature in the future as circumstances and conditions seem to demand."

The further circular of The American Society of Equity, dated September 24, 1906, will also be of interest to our renders: —

"It is deemed advisable that all growers of Essential Oils should know the market and price situations, this being the time that local buyers are acting with New York and other speculators to depress prices in order to cover short sales (futures) at too low figures, and stock up for speculative purposes. Now the public does not practically get any benefit out of these low prices to the growers and the grower is expected to rush in with his oil and sell at a lower price than he should in order to carry out the scheme to fill the pocket of the speculator.

At the Kalamazoo meeting September 5th, a price of from $ 2.75 to $ 3.00 was recommended and even higher prices justifiable, taking into consideration the consumption, cost of growing, shortage of crop and other natural disadvantages to the grower, local buyers and representatives of New York and other handlers of oils, were unanimous that $ 2.75 to $ 3.00 was not too high to the grower and only equitable for peppermint to the grower this season. Buyers admitting that the grower should have received $ 2.50 for last year's crop. It has turned out, however, that speculators will speculate as long as the grower will lay himself liable to speculation by being unorganized and uneducated as to the tricks that are played upon him, making the farmers the dupes of all others.

The plan at present is to scare the grower into selling his oil for a low figure, telling him the price is going down, and that there is more oil grown than was expected, staying away from the grower making him believe they do not want oil or any other story to scare in the oil, so the buyers have chopped from $ 2.75 to $ 2.40. Now candidly is this not a pernicious practice and should not every grower set himself against such practices and systematic robbery? New York papers read about like this: "While prices on peppermint are lower, the New York selling prices are unchanged". So you see it is like the millers, no matter how low wheat goes, the price of flour remains about the same.

There is surely a remedy for the frowners, and that is organization. As the crop is short and so admitted by all who read and are in touch with the situation a little bit, follow the plan of the American Society of Equity, hold your oil until the demand comes. Every pound of oil sold at a low figure will stand against the grower until consumed, and even the buyers may claim New York has lots of oil in stock. New York advices this summer have been about like this: Peppermint did not winter well; old stock short; prices higher.

This was when they were selling. Why don't they carry out their declarations and give the growers some benefit of the true situation?

No oil is being sold to speak of where growers are organized and now it rests with the growers to take care of themselves by simply holding for the price until the demand comes, which will not exceed 60 days, as not one tenth of the oil needed has been bought nor is in stock, and above all things do not be scared into throwing away your hard earnings. Come together and talk over the matter. Read up-to-date literature and get the true situation of the markets and prices of all farm products. Wayne and Seneca counties, New York, report only half crop.

Muskegon county, Michigan which has been known to have 60 000 pounds has only 10 000 pounds this season. Growers in all mint growing districts report short crop more or less, with but few exceptions. Conditions have been bad most of the summer and so reported in farm papers where they had the truth, one paper reports 50 pounds to the acre average. This is preposterous and never was known, except here and there a little. Indiana has suffered more than Michigan, these are facts and generally admitted by those who know.

Now get a hustle and get organized, take membership in the Society, including the Essential Oil branch only $ 2.00 per year, giving you information from time to time and the official paper, Up-to-Date Farming, published at Indianapolis, Ind., in the interests of profitable prices on all farm crops.

Remember if anything is done to help the farmer, he must attend to it himself and he will always be duped until he does it.

October 11th — This circular has been withheld from going out to learn if possible the cause of the depression in the market. The foregoing are the facts from reliable authority. "Some speculators in the East as well as West depressed the market for the very purpose of lowering it, and partly to the fact that a number of small dealers as well as growers made a large number of offers promiscuously, offering the same amount of oil to a number of houses which further hurt the market. The conditions accordingly are very unsatisfactory". What has been said in this circular is all in order and a good demand must come, as all admit the crop is much less than last year.

For information or membership write to any of the undersigned,

T. J. G. Bolt, Ravenna, Michigan,
Pres. and Chairman of Board of Essential Oil Branch.
R. E. Osborn, Secretary, Sherwood, Michigan.
Geo. C. Wattles, General Organizer, Sherwood, Michigan.

In the opinion of our New York branch, too much importance should not be attached to these resolutions.

Peppermint Oil, English. The sum total of the reports from the English peppermint districts is this, that this year on the average only one third of a normal harvest must be reckoned upon, as the great heat and drought during the spring have had a very injurious effect on the development of the plants. As a consequence the prices have advanced to about 34/- per lb., and a further rise in the course of the next few months may be expected, although the consumers at these high prices may possibly show great reserve. Fortunately we have still at our disposal the bulk of our last year's purchases, so that for the present we can be satisfied with a comparatively slight advance in our quotations. In offers for delivery during next year, the rise has of course to be taken into account.

Peppermint Oil, French. In continuation of some information which we gave in one of our last Reports[1]) on French peppermint oil, we give now a short description of an oil distilled by ourselves at our Barrême factory. The crude oil had a rather yellow colour and possessed a fine peppermint aroma, especially when diluted; by means of rectification a colourless distillate was obtained. d_{15° 0,9198; α_D — 9° 16′; 10,2% ester menthol; 48,9% total menthol; 3,9% menthone; soluble in 1,2 and more vol: 80 per cent. alcohol, when more than 3 vol. were added, opalescence.

As already mentioned by us before, the French oils are very popular in France.

Peppermint Oil, Japanese. The estimates of this year's harvest which reached us from our friends in Japan at the end of June, differed from each other to a not inconsiderable extent, inasmuch as the lowest mentioned 240000 kin, and the highest 265000 kin. The mean of the various statements divided over the different provinces is as follows: —

Bingu Bitchiu, etc.	150000 kin
Yonezawa . . .	25000 „
Hokkaido . . .	80000 „
total	255000 kin crude oil.

To this must be added 60000 kin stocks remaining over from last year, so that a total of about 315000 kin will be available for consumption, i. e. about 390000 lbs. Now if it were taken into consideration that important stocks of peppermint oil and menthol are still held in Europe, there appeared to be for the present no grounds for anticipating higher prices than last year. As the peasants, according to experience, are inclined to spread false rumours about the first cut, the above estimates had hardly reached the European market when reports sprang up that the fields had suffered heavily from the drought. Although subsequent information was again more favourable, the sellers showed great reserve, and fresh supplies were all the less urgently required as large stocks were still on hand; and as a smaller demand for consumption is made during the summer months, both purchasers and sellers assumed an observant attitude. The second cut took place under favourable weather-conditions, but in July and August rumours were set afloat of a threatening failure of the harvest in the American peppermint districts, so that the bulls succeeded in starting a strong upward movement of the market in

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[1]) Report April **1905**, 62.

August, and in driving up the prices of menthol in Europe to 9/- and of oil to 6/-. Since then the quotations have here again become somewhat weaker, and recently menthol is again quoted for forward shipment at 7/9, and oil at 5/9. As the rice-harvest in Japan this year has had very favourable results, the producers naturally ride the high horse, and are enabled to follow the course of events rather quietly without having to realise their peppermint products. The majority of the Japanese banks, moreover, is at any time ready to advance money on these products, and for this reason there is no great anxiety to procure the ready cash which may be wanted.

How the situation will shape itself further will depend now as before chiefly upon the attitude of the speculators. Their proved pertinacity may possibly succeed in keeping the prices at the present level, the more so, as according to the reports received, a deficiency in the American peppermint harvest would scarcely be surprising.

Peppermint Oil, Saxon. Thanks to the favourable weather-conditions which prevailed this year especially in our neighbourhood, and which led to exceptionally rich results in the harvest of all agricultural products, our own peppermint plantations in the vicinity of Miltitz have given very satisfactory results both in point of quality and quantity. This time the plants were free from the troublesome fungus-disease, a factor of great importance in the yield and the fine quality of the oil. It is well known that with regard to fineness of aroma our Saxon distillate stands unquestionably at the top of all peppermint oils and enjoys undivided support especially from the manufacturers of fine peppermint preparations.

Oil of Persea gratissima. The distillate from the leaves of a specimen of *Persea gratissima* Gaertn. growing in the garden of the Hôtel de la Californie at Cannes, which we received from Mr. Jean Gras of Cannes, was an oil with a very faint yellowish green colour, bitter taste, and an odour reminding of anise and remotely of estragon oil. It is known in the South of France under the name of *Essence d'Avocatier.* The oil had the following properties: d_{15° 0,956; $\alpha_D + 2^\circ 22'$; n_{D20° 1,51389; ester no. 3,8; ester no. after acetylation 18,9. The oil was soluble in 6 vol. 80 per cent. alcohol, with slight cloudiness and separation of paraffin; it formed a clear solution with about $^1/_2$ and more vol. 90 per cent. alcohol. In a freezing mixture it only became slightly cloudy, but did not congeal. On fractional distillation *in vacuo* (at 5 mm. pressure) there passed over: up to 83°, about 8%; from 83 to 84°, 71%; from 84 to 85°, 6%. The residue on distillation (about 15%) had a yellowish colour, and solidified partly when cooled.

The oil of *Persea gratissima* Gaertn. had already been examined in our laboratory in 1894[1]). At that time methyl chavicol was already recognised as the principal constituent of the oil. Although the conversion of this substance into anethol by heating with alcoholic potash did not then succeed, owing to the breaking of the vessel, it was yet possible to obtain anisic acid of the m. p. 183°, by oxidation of a small quantity of the oil thus treated with potassium permanganate. The renewed examination has confirmed the presence of methyl chavicol as principal constituent of the oil. Besides this, d-pinene was detected in the first runnings of the oil (b. p. to 83° at 5 mm. pressure; $a_D + 23°45'$). When distilled once at ordinary pressure over sodium, the bulk of this fraction passed over between 157 and 165°. By the action of amyl nitrite and hydrochloric acid in a solution of glacial acetic acid, pinene nitrosochloride was produced from it, whose benzylamine compound, after being once recrystallised from alcohol, showed the m. p. 123°.

The principal fraction of our oil had the peculiar odour of methyl chavicol, and also very nearly the properties of the pure body: $d_{15°}$ 0,9712; $a_D \pm 0°$; $n_{D16°}$ 1,52243; b. p. 83° (at 5 mm. pressure). By heating it for one hour with alcoholic potash, the bulk of the oil was converted into anethol solidifying at + 13,8°. Heating this crude anethol once more for one hour with caustic potash, raised the sol. p. only to + 14,2°. This product when distilled *in vacuo* (3 mm. pressure) passed over entirely between 85 and 87°. The principal fraction (b. p. 86,9 to 87,2°, 3 mm. pressure) had the pure taste and odour of anethol, and solidified at + 17,7°, whilst the portions first passed over only solidified at + 8,6°, and consequently still contained some methyl chavicol.

The fraction of the last runnings of the original oil (b. p. 84 to 85° at 5 mm. pressure) when distilled once more passed over almost completely at 80° (5,5 mm. pressure), and had $d_{15°}$ 0,971; $a_D \pm 0°$; $n_{D15°}$ 1,52278. It did not solidify in a freezing mixture, and therefore consisted also entirely of methyl chavicol, which was also proved by oxidation. When treated in the cold with 1 per cent. permanganate solution, it yielded first of all a solid acid, which showed still an indistinct melting point. It commenced to soften at 81°, but was only completely melted at about 160°. By fractional crystallisation from hot water two acids could be isolated from it, of which one (which appeared to be formed in the bulk, and which was readily soluble in water) formed colourless leaflets with a silver lustre, which finally melted between 84 and 85° (homoanisic acid = methoxyphenyl acetic acid). The other acid produced in smaller quantity, and more

[1]) Report October **1894**, 69.

difficultly soluble in water, formed long colourless needles, which melted not quite distinctly at 180° (in any case anisic acid, whose melting point should be at 184°). The conversion into anethol, and the occurrence of homoanisic acid as principal product of the oxidation with dilute permanganate solution in the cold, would therefore appear to prove, that the principal constituent of the oil examined is methyl chavicol.

The distillation-residue of the oil (about 15 %) represents a yellowish thick liquid, which reminded in the odour somewhat of sesquiterpenes. The available quantity was not sufficient for a more detailed examination. But by treating it with 80% alcohol, a considerable quantity of a paraffin could be isolated from it forming greasy needles with a silky lustre, which after recrystallisation from absolute alcohol melted at 53 to 54° (not quite distinctly).

The oil of *Persea gratissima* Gaertn. therefore consists for by far the largest part of methyl chavicol, and further of d-pinene, and paraffin-like substances.

Petitgrain Oil, Paraguay. When we reported on this article a year ago, we were under the impression that the difficulties in the supply would increase from year to year, as nobody would enter into binding contracts for the supply of this oil in any quantity worth mentioning, owing to the uncertain political situation in Paraguay. But no one could think that such a catastrophe as that which has taken place during the last few months, would break so suddenly over this oil which is of such great importance for the perfumery-trade. The production has ceased completely, and as moreover, owing to the failure of the orange-blossom harvest, the prices of neroli oil had to be raised to such an extent, there has arisen such a strong demand for the cheap substitute that the quotations gradually advanced from about 14 marks per kilo in October 1905, to 40 marks per kilo. Even at the last-named figure but a few kilos are available, and as new supplies, as already mentioned, cannot be expected, it is quite possible that the end of this misfortune is not yet in view.

With regard to the causes of this calamity, stress must be laid in the first place on the political situation of the country, which has brought about a state of affairs in the industry which promotes everything but a favourable development. The quarrels between the various parties, the care for their personal safety, and last not least the state of siege proclaimed as a last resource, have induced a large number of useful workmen to emigrate, and this has had the effect of doubling or trebling the wages. We also hear that, in addition to the above, such a severe drought has prevailed in the forests during the last few months that the water required for the distillation has not been available. The situation is judged from another point of view by R. v. Fischer-

Treuenfeld, who in his recently published excellent work "Paraguay in Wort und Bild" says: —

> "Although numerous wild-growing orange-forests are still in existence, they are nowadays already removed from inhabited villages, owing to the destructive harvesting method. The harvest takes place all the year round, but chiefly in the months from October to April. The trees are cut down about 2 inches above the ground, and the leaves and young fruit are distilled on the spot, the wood being used for heating the apparatus. Indolence and vandalism have thus led to the destruction of extensive orange-forests; in recent times the Authorities are taking pains to prevent the cutting down of the trees, and to regulate the harvests by law. For this reason the prices of the essential oils have advanced, and it is becoming more and more difficult to procure the product."

In view of these unfavourable conditions, further surprises in the near future may be anticipated.

The above-mentioned work also gives a summary of the export of petitgrain oil from Paraguay issued by the Chamber of Commerce of Asuncion, which we quote here for the sake of its interest: —

	1899	1900	1901	1902	1903
kilos	6106	9545	17834	19436	25176
value marks	48848	76360	107000	116616	146531

Pine-needle Oils. Unfortunately, the difficulties in obtaining supplies of pure normal oil of *Pinus pumilio* have now entered upon a new stage. Our old trustworthy purveyors, who were compelled to enlarge their distilling plant considerably, partly owing to the increased demand, have lately supplied an oil which — although its purity cannot be doubted — yet in its physical constants differs from that previously supplied by them, so that we were forced to amend our requirements regarding quality.

The properties which we had up to the present required in oil of *Pinus pumilio* were: d_{15° 0,865 to 0,875; α_D — 4° 30′ to — 9°; ester-content (bornyl acetate) 5 to 7 %. The British Pharmacopœia had specified practically the same data, as it required for oil of *Pinus pumilio* the following constants: $d_{15,5^\circ}$ 0,865 to 0,870; $\alpha_{D\,15,5^\circ}$ — 5° to — 10°; below 165° at most 10 % may distil over. According to our this year's experience, these limits appear to us to be too narrow, as unobjectionable distillates from various districts show this year not unimportant deviations, which are attributed to the abnormal weather conditions by distillers known to us as reliable. For example, we received oils distilled in the Tyrol, which were distinguished by a particularly low specific gravity and high rotation. The constants fluctuated between the following limits: d_{15° 0,8596 to 0,8629; α_D — 10° 57′ to — 15° 20′; ester-content 4 to 4,9 %; soluble in 4,5 to 6,0 and more vol. 90 per cent. alcohol.

Another distillate from Styria, on the other hand, was characterised by a lower rotation and a somewhat lower solubility. It had the

following properties: d_{15° 0,8705; $\alpha_D - 3^\circ 47'$; ester-content 4%; soluble in 8 vol. 90 per cent. alcohol.

As in the case of all these distillates any adulteration whatever is out of the question, it will be necessary to revise the limits fixed; for our part, we must for the present decline to fix definite figures as the material at our disposal does not yet appear to be sufficient for the purpose.

Oil from the needles of *Abies alba* is again in stock in abundant quantity, but the fine Swiss oil from the cones (*Ol. templini*), the manufacturing season of which takes place in the last months of the year, may possibly only be obtainable this year with great difficulty. Although the formation of the young sprouts looked very promising this spring, the trees now only carry such a small quantity of cones, that it will scarcely pay to gather them. For this reason the prices will have to be raised in proportion.

It is all the more satisfactory that we are able to state that the Siberian pine-needle oil finds favour with a constantly growing number of consumers, who are utilising it for their purposes on account of its powerful characteristic odour, and not the least on account of its advantageous price. Our informants report that the distillation takes place in the summer and autumn, and that orders placed in the spring and summer can be executed to any extent. Only in the autumn and winter it is often difficult, and occasionally impossible, to procure the oil, owing to the difficulties in the transport caused by snow and ice. The producing-district is in the Government Wjatka, whilst Siberia itself supplies only small quantities which cannot compete owing to the high cost of transport. The new railway Wjatka-Wologda-St. Petersburg has meanwhile been opened for traffic, and this route will be the more advantageous one for the transport of the oil. There are no difficulties of any kind which would prevent the supply of this oil in any desired quantity.

A distillate from the needles of *Pinus halepensis* Mill. originating from Algeria, had the following properties: almost colourless; d_{15° 0,8643; $\alpha_D - 3^\circ 22'$; acid no. 1,3; ester no. 21,2 = 7,4% ester, calculated for bornyl acetate. The oil has accordingly a certain similarity to the oil of *Pinus pumilio*, which it also approaches in respect of the odour.

In continuation of his examinations of the essential oil of the shoots of *Pinus maritima* Mill.[1]), E. Belloni[2]) detected the presence of l-borneol, by means of Tiemann and Krüger's[3]) phthalic anhydride process. The l-borneol obtained melted at 205°. Possible deviations of his present values from those previously obtained are

[1]) Comp. Report April **1906**, 57.

[2]) Boll. Chim. Farm. **45** (1906), 185. Acc. to Chem. Centralbl. **1906**, I. 1552.

[3]) Berl. Berichte **29** (1896), 901.

attributed by the author to the various stages of development of the shoots, and to the different places of origin of the specimens.

Oil of Pinus Sabiniana Douglas. The oil from the turpentine of this conifer growing in California was first examined by Wenzell[1]. According to him it consists almost entirely of the hydrocarbon abietene. Thorpe[2] and others proved than Wenzell's abietene is normal heptane. The presence of a low paraffin hydrocarbon in conifer oils had up to that time not yet been observed, and for this reason it was believed by others[3] that the oil examined had been mixed with a petroleum fraction. As Thorpe examined a distillate which also originated from Wenzell's source, his examinations did not prove the genuine character of the crude material and the actual presence of heptane. In the meantime Kremers[4] has pointed out that there can be hardly any doubt as to the purity of the material examined by the above-named authors.

In order to become more closely acquainted with this interesting oil, we obtained from the manufacturers of abietene (Abietine Medical Company, Oroville, Cal., U. S. A.) the balsam serving as crude material. In the prospectus recommending abietene as "Butte-Tine" against all possible diseases, it is only stated with regard to the origin that it is obtained from the balsam of a pine which is only found in Butte Creek and Butte County, California. But from the above-mentioned information from Kremers the conclusion may be drawn that this pine is probably identical with *Pinus Sabiniana* Douglas.

The balsam represents a viscid, only just flowing brown yellow mass with a greenish glimmer, and with a not unpleasant odour reminding of sweet orange. It is soluble in alcohol, ether, benzene, and partly soluble in petroleum ether. Acid no. cold 156; sap. no. hot 179,05.

We obtained from the balsam by distillation with water vapour, 8,44 % almost water-white essential oil, and 91,3 % yellow brittle resin.

The oil had the following properties: d_{15° 0,6962; α_D — 0° 9′; behaviour on boiling: 97 to 98,5° 5 %; 98,5 to 99° 87 %; above 99° 8 %. The principal fraction of the b. p. 98,5 to 99° was optically inactive, had d_{15° 0,6880, and corresponded in its properties with those given by Thorpe for his heptane. We are therefore able to confirm the previous information on the essential oil of *Pinus Sabiniana.*

The portions of the oil boiling above 99°, could be split up by fractional distillation *in vacuo* into 7 fractions of not very uniform boiling points, which at 12 mm. pressure lay between 43 and 103°.

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1) Amer. Journ. Pharm. **44** (1872), 97. Pharmaceutical Journal III. **2** (1872), 789.
2) Liebig's Annalen **198** (1879), 364.
3) Comp. Gildemeister and Hoffmann, The Volatile Oils, p. 254.
4) Pharm. Review **18** (1900), 165.

All fractions showed optical lævorotation, with the exception of the last one which was dextrorotatory. The fraction in its boiling point corresponded to the terpene fractions, briskly absorbed bromine, with slight evolution of hydrobromic acid. A more detailed examination of the individual fractions was not made.

Oil of Pittosporum undulatum. F. B. Power and F. Tutin[1]) report on the constituents of the essential oil from the fruit of *Pittosporum undulatum* Vent. indigenous to South-Eastern Australia. The crushed fruit yielded 0,44 % oil which changed when kept for a prolonged time; d_{15° 0,8165; $\alpha_D + 74^\circ 4'$; insoluble in 10 vol. 70 per cent. alcohol. The fractional distillation yielded up to 165° 4 % d-pinene (nitroso chloride; nitrolbenzylamine, m. p. 123°). Between 173 and 180°, 75 % limonene passed over (tetrabromide, m. p. 104°), and between 200 and 225° a body which must probably be regarded as an alcohol, yielding on oxidation a ketone $C_9H_{14}O$ with a coumarin-like odour. Finally, between 263 and 274° there distilled an optically inactive sesquiterpene $C_{15}H_{24}$ (d_{15° 0,910; n_{D20° 1,5030), from which not a single solid derivative could be obtained, and which is not identical with any of the hitherto known sesquiterpenes. The molecular refraction showed that it is dicyclic, and has two ethylene linkings. There could further be detected traces of palmitic and salicylic acids, and a not determined phenol with a eugenol-like odour, and finally traces of esters of valerianic, formic, and other acids.

Rose Oil, Bulgarian. This year's distillation commenced at an exceptionally early date and has been accomplished under the most favourable weather-conditions, so that the fears, to which expression was given at the end of the previous season, have fortunately not been realised, and this time again the harvest has given an abundant result. The weather was throughout cool and not too dry, and as a consequence the distillation period lasted a very long time, which, as we know from our own experience, is very advantageous for the yield and for dealing with all the flower-material. According to our informants, this year's production reaches nearly 4600 kilos, which means about 470 kilos more than in 1905. Other reports speak of only 3761 kilos as compared with 3523 kilos last year. A fact is, that after the usual manœuvres for fixing the prices had been completed, the quotations have been maintained at the same level as in 1905, the producers doing everything possible to compensate themselves to some extent for the continuously growing manufacturing expenses. With the support of the Government, the manufacturers induced the Chamber of Industry and Commerce at Philippople to convene a con-

[1]) Journ. chem. Soc. **89** (1906), 1083.

ference of rose oil merchants and manufacturers for the 1st of July, at which broadly the following resolutions were passed: —

1. The rose oil producers are recommended to cultivate no white roses if possible, as they give a small yield and are generally inferior;

2. The Government to be applied to, to establish experimental fields at which the best conditions for the rose-cultivation and the protection against diseases, parasites, etc. are to be studied. Plantation experiments with all other possible aromatic plants to be also carried out on those fields;

3. Everyone to be free to distil roses by means of steam or other systems;

4. The Government to be requested to support in the most energetic manner the cultivation and distillation of all newly introduced aromatic plants;

5. The conference unanimously denounces the adulteration of rose oil and recommends the Government to use all means at its disposal to protect the purity of the oil. The conference recommends among others that the Government should exercise control over all distilling installations in which at least 100 000 kilos petals are used up. This controlled oil to be provided with an official seal after the manufacture and when exported; the control would therefore no longer be exercised by the custom-houses. In this manner the Government would force the small distillers to combine to a union of interested parties instead of competing with each other;

6. It is suggested to the producers that they should obtain officially tested thermometers, so that they may not be imposed upon when selling or collecting rose oil. The exclusive use of such thermometer to be impressed upon all communities and merchants.

The Postmaster-General to be requested to treat samples of rose oil as "samples without value" and not as parcels containing valuables for which a high rate of postage has to be paid.

We have had no opportunity yet to discuss with our informants in how far these resolutions can be carried out, and what the expected effect of these regulations on the rose oil trade is. For our part, we sincerely welcome every step which may be taken to improve the position of an article which in the true sense of the word must be called a victim of the adulterators.

Parry[1]) has had an opportunity of examining a considerable number of rose oils which had been adulterated in the most serious manner. The adulterators endeavour to take advantage of the experience that rose oil produced in a special manner behaves differently

[1]) Chemist and Druggist **69** (1906), 230.

from ordinary distilled rose oil, and they puff up their oils as "oils distilled by a special method". The abnormal pure rose oils are above all characterised by a high content of phenyl ethyl alcohol, which is obviously absent from the mixtures. According to Parry's experience, the ordinary Bulgarian rose oil has never a higher specific gravity than 0,855; it lies mostly between 0,850 and 853 (at 30°). Oils with a higher specific gravity which do not contain phenyl ethyl alcohol, should unconditionally be rejected. Parry quotes the constants of 15 samples adulterated in the coarsest manner; the values lay within the following limits: d_{30° 0,862 to 0,880; α_D —1° 10′ to — 3° 20′; n_D 1,4650 to 1,475; m. p. 20 to 22°.

Rose Oil, German. The harvest in our Miltitz plantations, to which we now as before devote our undivided attention (contrary to the rumours spread from certain quarters), was this year at last again carried on under very favourable weather-conditions, so that excellent blossom-material could be worked up, and in point of quantity also a result was obtained as had not been the case for years. Several new plantations laid out during the last few years gave for the first time a full yield, and the plants which had to be cut back in 1904 owing to the drought, have meanwhile recovered completely. On some days the fields afforded a quite imposing spectacle, and it gives us particular pleasure to be able to state, that especially in this year during the harvest time we had repeated opportunities of showing this fine view to friends who took an interest in this cultivation. Our new oil is of excellent quality, and we have also again at our disposal abundant quantities of rose-pomade and rose-water.

In our oil we determined the following constants: $d_{15^\circ}^{35^\circ}$ 0,8444; α_{D35° — 0° 23′; n_{D35° 1,46139; sol. p. + 30,8°; acid no. 4,3; ester no. 5,2; ester no. after acetylation 178,8, corresponding to 56,8 % $C_{10}H_{18}O$; paraffin-content about 42 %.

Rosemary Oil. The French distillate can again, as in 1905, be had very advantageously, but we are informed that the market suffers much from the competition of Spanish rosemary oils, and that as a consequence a number of manufacturers will no longer occupy themselves with the distillation. In our opinion the value of the Spanish quality is much overrated, for we have had before us a number of samples which could not come under consideration as substitutes of the French article, with regard to either their physical properties, or their odour. In spite of the low prices of the last-named oil, the Dalmatian producers still ride the high horse, and do not yet want to hear of a reduction of their prices as compared with 1905. The demand for their product is very brisk, which may be due to this, that the light camphor oil, used in the preparation of the notorious

cheap denaturating qualities, is no longer available in the same quantities as before, and that for this reason more pure rosemary oil is used for denaturating purposes. We have again secured a large share of the output and are thus able to meet every demand; but those interested in "cheap" rosemary oils, should apply to the firms who make a particular specialty of the production of such qualities.

E. J. Parry and C. T. Bennett[1]) publish the result of examinations with regard to the rotation of Spanish rosemary oil. As it had often been observed that Spanish rosemary oils had a lævorotation, this occurrence was attributed to adulteration. We also had, though only in a few cases, observed[2]) lævorotation in oils from a reliable source, and had already suggested the question, whether the requirement that the first 10 % of the distillate must also be dextrorotatory, could be upheld to its full extent, or whether a slight lævorotation of the first 10 % might be allowed, if the specific gravity were sufficiently high. Parry and Bennett now have obtained from an authentic source samples of rosemary, of which the herb was distilled in the laboratory of Wright, Layman & Umney. The examinations of the oils produced showed that rosemary oils of guaranteed purity may also be lævorotatory, and that moreover a dextrorotatory oil may yield lævorotatory fractions. In France the oil is always distilled from herb gathered after the blossoming period (February, March) and dried for about 8 days in the sun. In Spain, however, the distillation takes place all the year round, and both fresh and dried herb are used there as the case may be, which explains why the oils vary somewhat. In the dried state the leaves are readily separated from the stalks by threshing, but in the fresh condition this is impossible. The yield of oil from the fresh herb fluctuates between 0,4 and 0,75 %, that of the dried herb comes to up to 1 %; the last-named oil is also of better quality. The properties of three samples examined by the authors were: Spanish oil from the leaves only: d 0,917; $\alpha_D + 5^\circ 30'$; ester-content (bornyl acetate) 3,20 %; total borneol 19,7 %; α_D of the first 10 % of the distillate $- 1^\circ$. French oil (leaves and stalks): d 0,897; $\alpha_D - 8^\circ 30'$; ester-content (bornyl acetate) 3,0 %; total borneol 10,9 %; α_D of the first 10 % of the distillate $- 12^\circ 30'$. French oil (leaves): d 0,914; $\alpha_D - 3^\circ$; ester-content (bornyl acetate) 3,6 %; total borneol 18,5 %, α_D of the first 10 % of the distillate $- 10^\circ$. The results show therefore that the lævorotatory constituent (l-pinene) is represented in larger quantity when the stalks are distilled along with the leaves, and that the stalks contain less oil; and further, that oil obtained from care-

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1) Chemist and Druggist **68** (1906), 671.

2) Report October **1904**, 82.

fully picked leaves contains lævorotatory fractions. Finally it is evident that oil from the leaves only has a higher borneol-content, and consequently also a finer odour.

On the strength of Parry and Bennett's observations, the "Chemist and Druggist"[1]) finds fault with the observation[2]) made by us when discussing the Spanish Pharmacopœia, that pure rosemary oil is dextrorotatory, and that lævorotation points to adulteration with French oil of turpentine. We would reply to this that these statements are based upon the observations made up to the present, according to which the pure lævorotatory oils in commerce belong to the exceptions. But when the Spanish Pharmacopœia excludes the dextrorotatory rosemary oils, it is in direct contradiction with the facts. In any case it will be well to continue exercising care in dealing with lævorotatory rosemary oils.

The fact that the time of the year also influences the quality of the oil contained in rosemary, appears to have been proved by A. Birckenstock[3]). In order to show that rosemary plants from the same ground and soil (St. Bauzille de Montmel, Hérault), worked up under exactly the same conditions, yield oils of different rotatory powers, three distillations were carried out, viz., in the spring, summer and autumn. On the other hand, samples of rosemary from Cannes (Alpes Maritimes) were distilled in the spring and summer. The authentically pure oils showed the following optical behaviour: —

	α_D of the oil	α_D of the 1st fraction 10%	α_D of the 2nd fraction 16%	α_D of the 3rd fraction 16%	Residue
Hérault, spring (April) . .	$+6°32'$	$-4°10'$	$-3°10'$	$-1°42'$	$+13°6'$
Hérault, summer (July) . .	$+8°17'$	$-0°28'$	$+0°50'$	$+2°52'$	$+13°16'$
Hérault, autumn (end of Nov.)	$+11°$	$+1°58'$	$+2°6'$	$+3°15'$	$+16°57'$
Cannes, spring (13 April) .	$-0°57'$	$-13°38'$	$-11°35'$	—	$+16°57'$
Cannes, summer (end of June)	$+5°57'$	$-2°4'$	$-1°16'$	$+0°30'$	$+11°7'$

In the case of Spanish rosemary oil the case is this, that the rotation has always been found to the right, but has decreased considerably in the autumn. Both oils, Spanish and French, show fluctuations in the pinene-content, but the former contains d-pinene preponderatingly in the spring, and is in that season richer in pinene than in the autumn, which may be concluded from the low specific gravity ($d_{15°}$ 0,8851) of the spring oil. Birckenstock's examinations therefore allow the conclusion to be drawn that the view, that lævorotatory rosemary oils are adulterated with turpentine oil, does not

[1]) Chemist and Druggist **69** (1906), 137.
[2]) Report April **1906**, 85.
[3]) Moniteur scientifique Quesneville, May **1906**.

always apply, if the specific gravity of the oil in question is sufficiently high.

We are not yet prepared to express a definite opinion on what has been stated above, as the material upon which the examinations are based does not appear to us sufficiently voluminous to consider the question as definitely solved.

L. Vanino and F. Hartl[1]) have found that some essential oils, such as rosemary oil, which was formerly used for the manufacture of Aurum potabile, and oil of turpentine, are eminently adapted for the production of gold hydrosol. Solutions containing more than 0,0181 % gold, are, however, not suitable. The turpentine oil employed must be pure.

Rue Oil. Birckenstock's work[2]) already quoted under lavender oil also deals with oil of rue. French oil of rue (*Ruta graveolens* L.), as is well known, differs from the Algerian oil by its congealing point. Both contain about 90 % ketones, but the French oil almost exclusively methylnonyl ketone (m. p. + 15°), and the Algerian methylheptyl ketone (m. p. — 16°)[3]). Morphological distinguishing characteristics of the two plants do not exist. Birckenstock now has distilled Algerian rue oil at three different vegetation periods, and has thereby made the interesting observations that the differences in the compositions are only attributable to the season in which the oils are distilled Algerian rue oil showed exactly the same composition and the same properties, when it was, like the French, distilled in the autumn. This work of Birckenstock's is supplemented by H. Carette's[4]) examinations, who states that two kinds of rue oil are produced in Algeria, which differ in a marked degree from each other, and of which one is designated "summer rue oil" ([from *Ruta montana* L.], consisting chiefly of methylnonyl ketone, sol. p. between + 5 and + 8°), and the other "winter rue oil" ([from *Ruta bracteosa* L.], almost exclusively consisting of methylheptyl ketone, sol. p. — 18°). A rue plant described as *"rue de Corse"* was also found by Carette to be identical with *R. bracteosa*; the sol. p. of the oil lay at — 15°, but it appears to contain, in addition to methylheptyl ketone, large quantities of methylnonyl ketone. According to Carette, the essential rue oils of various origins can therefore be distinguished by isolating their ketones with sodium bisulphite. An adulteration with turpentine oil or petroleum can at once be detected by the fact that pure rue oils,

[1]) Berl. Berichte **39** (1906), 1696.
[2]) Moniteur scientifique Quesneville, May **1906**.
[3]) Report October **1901**, 47; comp. also Report April **1901**, 51.
[4]) Journ. Pharm. et Chim. VI. **24** (1906), 58.

whatever may be their origin, all dissolve in 2 to 3 vol. 70 per cent. alcohol, whilst the adulterated oils do not dissolve.

Sandalwood Oil, East Indian. The quotations have remained unchanged; the demand continued to be brisk, but there are indications that the prices of sandalwood-oil capsules, forced down by senseless competition, are such that the manufacturers of the capsules are beginning to be somewhat more reserved in their purchases. It appears that large stocks of oil and wood in London and Hamburg are still in the hands of the producers, so that any particularly animated interest in the auctions in India, which began on November 17th, as per particulars hereafter, was not to be anticipated. Nevertheless, according to cables reccived until going to press, the first three sales have started off at very high prices, paid chiefly by natives, but it remains to be seen whether they will last.

Statement of the quantities of Sandalwood to be sold between November 17th and December 17th: —

Date	Auction	Quantity		
		Tons	cwts.	lbs.
Nov. 17	Fraserpet	230	3	44
„ 19	Hunsur	500	2	—
„ 22	Seringapatam	303	15	28
„ 26	Bangalore	82	6	87
„ 29	Hassan	200	1	84
Dec. 3	Chikmagalur	308	5	—
„ 6	Tarikere	256	1	84
„ 8	Shimoga	487	4	49
„ 13	Sagar	175	12	—
„ 17	Tirthahalli	178	11	36
	Total:	2722	3	76

We read in the "Chemist and Druggist" that Parry[1]) has also detected adulterations of sandalwood oil capsules, and has found that the adulterant was West Indian sandalwood oil, which, as is well known, is about three times as cheap as East Indian. Yet we would point out that the designation *Schimmelia oleifera* Holmes, mentioned by Parry as the mother-plant of West Indian sandalwood oil, no

[1]) Chemist and Druggist **68** (1906), 951; comp. also Report October **1903**, 63; October **1904**, 83; April **1905**, 72; April **1906**, 61; also Gildemeister and Hoffmann, The Volatile Oils, p. 342.

longer applies, but that the name *Amyris balsamifera* L.[1]) must be substituted, under which the plant had already been identified previous to Holmes' examinations.

Savin Oil. In our last Report we discussed on p. 62 among others also a work by Umney and Bennett, in which it was pointed out that French oil of savin is usually not obtained from *Juniperus sabina* L., but from *Juniperus phoenicea* L.; the oil behaves approximately as a genuine savin oil to which oil of turpentine has been added. As a matter of interest we quote here the properties of an oil from the leaves of *J. phoenicea*, which we received from a business friend in Cannes: d_{15° 0,8643; $\alpha_D + 7^\circ 20'$; ester no. 1,5; ester no. after acetylation 6,6; soluble in 6,5 and more vol. 90 per cent. alcohol.

As *Juniperus thurifera* var. *gallica*, described more in detail by Holmes[2]), which is indigenous to the South of Spain and Algeria, also occurs in the departments Hautes-Alpes and Isère, and is often confounded with *Juniperus sabina* L., it is also quite possible that the oil of this species is employed for adulterating oil of savin, — a matter to which we would here call attention.

Shellac Oil. A. Etard and E. Wallée[3]) supply some interesting information on the dry distillation of shellac which, when mixed with an equal weight of sand and distilled, yielded 6 % gaseous portions, 72 % liquid distillate, and 22 % coke-like residue. The distillate immediately separated off water; there floated on it a brown, viscid, faintly fluorescent oil (d 0,975), which represented about 52 % of the shellac. 40 % of the oil dissolved in dilute alkalies. Hydrochloric acid separated off from it an oil with a strong odour of fatty acid; the analysis showed pure oleic acid, and caproic acid and sebacic acid were obtained as further products of decomposition. The portion insoluble in alkalies contained terpenes; distillation with water vapour resulted in a hydrocarbon (?) of the b. p. 170 to 175° (possibly dipentene), and a terpene $(C_5H_8)_n$ of the b. p. 235 to 240° which was soluble in alcohol and benzene, but insoluble in glacial acetic acid. The residue of this water vapour distillation contained a polyterpene (b. p. 310°) and a saturated hydrocarbon $C_{32}H_{66}$ (m. p. 61 to 62°, b. p. about 360°). On the strength of this examination, shellac appears to be a not very stable oleate of a continuous series of polyterpenes.

Solidago Oils. With reference to the two solidago oils described in our last Report[4]) we would here give the supplementary information that according to a communication received from an authoritative

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[1]) Gildemeister and Hoffmann, The Volatile Oils, p. 486.
[2]) Pharmaceutical Journal **75** (1905), 830.
[3]) Compt. rend. **140** (1905), 1603.
[4]) Report April **1906**, 62.

source, the ordinary commercial product known under the name "oil of golden rod", does not originate from a definite species of solidago, but is a distillation-mixture from the most diverse solidago species, which are very numerously represented in the United States. A. Gray[1]) describes in his Flora of the Northern United States alone 42 solidago species.

The full name of the mother plant of the other solidago oil mentioned in our Report, is, according to Gray, *Solidago nemoralis* Aiton.

Spearmint Oil. After a long time we have once more received Russian spearmint oil[2]), which, as is well known, has a much lower specific gravity and a lower optical rotation than the American and German distillates, and differs from these chiefly by its high linalool-content, and its low content of carvone. We reproduce here, on account of its interest, the constants of the oil, which has a stale feeble odour like spearmint: d_{15° 0,8873; α_D — 25° 16′; n_{D20° 1,47078; acid no. 1,1; ester no. 15,9; soluble in 2,2 vol. and more 80 per cent. alcohol; soluble in 1 and more vol. 80 per cent. alcohol.

Another Russian distillate had the following properties: d_{15° 0,8884; α_D — 25° 20′; n_{D20° 1,47088; acid no. 0; ester no. 15,1; soluble in 3 and more vol. 70 per cent. alcohol. Contrary to these, the American and German distillates have the following properties: d_{15° 0,92 to 0,94; α_D — 36 to — 48°; soluble in about 1 vol. and more 80 per cent alcohol; the dilute solution has a faint opalescence.

The Russian oil can scarcely be regarded as a substitute to the American spearmint oil which after a long period of high prices is now lowering to a reasonable limit. The crop is said to be a good one.

Spike Oil. The extraordinary drought which has this year destroyed all hope for normal prices of lavender oil, has unfortunately also been fatal for spike oil, and although prices of 12 francs, such as ruled last year, need not be paid now, unobjectionable oil can scarcely be bought below 9 to 9.50 francs per kilo. Although such prices render the use of this article prohibitive for many purposes, the position of the lavender-oil market is a guarantee that there will be no lack of persons interested in spike oil.

In his work on the influence of cross-fertilisation between lavender and spike on the quality of their essential oils, A. Birckenstock[3]) also discusses the differences existing between pure spike oils when

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[1]) Asa Gray, Manual of the botany of the Northern United States, p. 246.

[2]) Comp. Gildemeister and Hoffmann, The Volatile Oils, p. 653; Bericht April **1889**, 23 and Report April **1898**, 45.

[3]) Moniteur scientifique Quesneville, May **1906**; comp. also the corresponding article under lavender oil, p. 43.

the plants are grown in different districts. According to this Birckenstock distinguishes the following groups: Ardèche, Hérault, Drôme, Gard, Basses-Alpes, Alpes-Maritimes, and Var. Whilst according to the author, the first named group represents the spike type proper, and yields oils of the following properties: d_{15° 0,918 to 0,921; $\alpha_D + 7^\circ 48'$ to $9^\circ 36'$; α_D of the first 10 per cent. of the distillate $+ 8^\circ$ to $+ 10^\circ$; ester-content 4 to 5 %; alcohol-content 21 %; soluble in 3 vol. 67 per cent. alcohol, — the "Var" group already closely approaches the lavender type: d_{15° 0,9035 to 0,905; $\alpha_D - 1^\circ 10'$ to $\pm 0^\circ$; α_D of the first 10 per cent. of the distillate $+ 2^\circ$; ester-content 2 to 3 %; alcohol-content 20 to 32 %; soluble in 5 to 6 vol. 60 per cent. alcohol. The other groups represent intermediate stages. Specific gravity and rotation therefore become less, whilst alcohol-content and solubility increase; inasmuch as the borneol greatly preponderating in the "Ardèche" type is gradually substituted towards the "Var" type by linalool and geraniol. The lævorotation of the last-mentioned oil is also remarkable, but Birckenstock considers that up to $- 1^\circ 10'$ this is still normal, provided that the first 10 per cent. of the distillate rotate to the right.

The above statements agree only partly with the observations hitherto made, according to which pure spike oil has the following constants: d_{15° 0,905 to 0,915; α_D to the right[1]); α_D of the first 10 per cent. of the distillate also to the right. Further detailed studies are wanted to solve this question definitely.

An adulteration not observed with spike oil up to the present was recently detected in our laboratory. The oil behaved as follows: d_{15° 0,9282; $\alpha_D + 5^\circ 56'$; α_D of the first 10 per cent. of the distillate $+ 6^\circ 46'$; ester no. 8,1; soluble in 2 and more vol. 70 per cent. alcohol. The high specific gravity was particularly striking, but the oil was also suspected on account of its peculiar smell. The further examination showed that nitrobenzene had been added to the oil, which was isolated from it by fractional distillation, and was further identified by conversion into aniline. This adulteration cannot be called very clever.

Star-anise Oil. This article has been greatly neglected during the last few months; speculative enterprise was entirely absent, yet there appears to be no stock of excess production worth mentioning, as the market has maintained itself with slight fluctuations at 5/2 to 5/5 cif. Hamburg. Tonquin oil was practically not offered at all, and the parcels which came on offer were quoted at prices which were entirely out of proportion to the China oil. The latter, moreover, has during the last few years left nothing to be desired in point of quality.

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[1]) Comp. also Report April **1904**, 83.

Oil of Thuja leaves. We abstract the following from a communication from E. Ayer[1]) on this oil which originates from the white cedar, *Thuja occidentalis* L. The oil of *Thuja occidentalis* is, in spite of its totally different properties, often confounded with that of *Juniperus virginiana* L., the red cedar. In Pennsylvania and the States to the North of it, the white cedar is generally called "swamp cedar". The leaves and twigs of *Thuja occidentalis* are said to contain up to 1 % oil. Since many years the oil is distilled more especially in the Northern and Eastern districts of Vermont, but the result of the distillation and particulary the quality of the oil are dependent upon various circumstances. The trees which are on all sides open to the sunlight are the best. The distilling plant is frequently of a very primitive character. The most important function during the whole process is the filling of the stills with the branches and leaves, as gaps must if possible be avoided in the distillation. The higher the steam pressure, the richer the yield. Sometimes oil of thuja leaves is water-white, but often, when the trees have grown in shady places, it is dark-coloured. Cold weather affects the oil-content of the wood, but not that of the leaves. Thuja leaf oil forms an important constituent of the ointments employed against scurvy, rheumatism, etc.; it is even used against cancer, and its purity is consequently the most important factor. In spite of this it is frequently adulterated with turpentine oil and petroleum, chiefly by the middlemen. The annual production of this oil is difficult to estimate, as it is subject to large fluctuations.

Turpentine Oil. From the results of the fractional distillation of American and French oils of turpentine, B. Ahlström and O. Aschan[2]) draw the conclusion that turpentine oil contains, in addition to pinene, a further terpene (or perhaps more than one) which has a rotatory power opposite to that of the pinene belonging to it. Not even the pinene fractions proper (155 to 156°) consisted exclusively of pinene. The hydrochlorides of pinene produced from the two oils pointed to the probability that it was a question of a pseudo-pinene according to Semmler. But the fact that the quantities of hydrochloride obtained from the higher fractions diminished considerably, whilst pseudo-pinene should give addition-products identical with those of pinene, rendered this assumption untenable. Further examinations now showed that the higher pinene fractions no doubt contained larger quantities of pseudo-pinene, but that this is not the only foreign constituent of these fractions. Aschan assumes therefore that possibly cymene or limonene may be present, although

[1]) Oil, Paint and Drug Reporter, June 25, **1906**, 17.
[2]) Berl. Berichte **39** (1906), 1441.

he does not consider the former as probable. Finally, the presence of camphene in the higher pinene fractions may also be thought of.

O. Aschan[1]) fractionated the turpentine each from *Pinus silvestris* L. and from *Pinus Abies* L.; both passed over below 180° with the exception of a very small residue. The semi-liquid turpentine from *P. silvestris* yielded 9,2 % terpenes, the somewhat harder turpentine from *P. abies* (pine resin) only 4,5 %. The fractions obtained from these oils also point to this, that in the lower boiling portions other terpenes, besides pinene, must be present. The presence of a l-pinene in the balsam of *Pinus abies* L. has now been proved by Aschan's experiments, whilst the d-pinene, as already detected before, originates from Finnish, Swedish, and most probably also Russian turpentine oils from *Pinus silvestris* L. Furthermore, sylvestrene was detected with certainty in the balsam of *Pinus silvestris* L. Aschan believes, on the strength of the greatly increasing lævorotation of the higher fractions of the turpentine oil from *Pinus abies,* that a comparatively large content of l-limonene may be accepted, which occurs as dipentene dihydrochloride when hydrochloric acid is added. The detection of sylvestrene is all the more interesting to us, as we had already discovered this hydrocarbon before in German oil from the needles of *Pinus silvestris.*[2])

With regard to Swedish turpentine oil, I. Kondakow and J. Schindelmeiser[3]) communicate the following: the dextorotatory oil gave a fraction of the b. p. 153 to 160° ($\alpha_D + 22° 28'$), one of the b. p. 185 to 190° ($\alpha_D + 10° 20'$), and a small residue. There was present in the oil, in addition to sylvestrene and dipentene, a hydrocarbon of the b. p. 174 to 176° ($\alpha_D \pm 0°$; $d_{19°}$ 0,854; n_D 1,49013), which could not be made to combine with hydrochloric acid, and on oxidation with permanganate yielded oxyisopropylbenzoic acid (m. p. 155°). As moreover cymene sulphonic acid was identified by its barium salt, the hydrocarbon had to be considered as p-cymene. From the same oil a not yet identified hydrocarbon of the b. p. 145° was also fractionated off.

Mokievsky[4]) has made a study of the products of decomposition of turpentine oil which are formed during the heating in a sealed tube. The oil was heated to a very high temperature in the closed

[1]) Berl. Berichte **39** (1906), 1447 and 2596.
[2]) J. Bertram and H. Walbaum, Arch. der Pharm. **231** (1893), 290.
[3]) Chem.-Ztg. **30** (1906), 722.
[4]) Journ. russ. phys. chem. Ges. **36**, 913. Acc. to Chemist and Druggist **68** (1906), 617.

tube and the bodies thereby formed were separated. There were obtained: 1. gaseous portions, 2. liquids of different fractions, viz., of the boiling points 20 to 30°, 30 to 40°, 70 to 80°, 96 to 110°, and 135 to 145°. A large proportion of the substance remained unaltered, but a heavy high-boiling oil was also obtained. In the volatile portions ethylene and propylene were detected, whilst the fraction between 20 and 30° contained divinyl and various isomeric butylenes. The fraction between 30 and 40° consisted almost entirely of isoprene and trimethyl ethylene. The next fraction (70 to 80°) contained 10% benzene, and various hydrocarbons with open chain, chiefly dimethylisopropyl ethylene; in the fractions 95 to 145°, toluene and different xylenes were present.

In our last Report[1]) we have already briefly described W. Vaubel's[2]) brominating method, and also called attention to the objections raised by Holde and Herzfeld. Vaubel now has recently[3]) published modifications improving his process. But Herzfeld[4]) also objects to these, as in his opinion adulterations which could at once be detected by means of the refractometer could not be determined by Vaubel's method. For this reason Herzfeld recommends that in the examination of turpentine oil the refractometric test should always be made first.

R. Böhme[5]) recommends the following method for the estimation of petroleum, petroleum distillates, and benzene, in oils of turpentine and pine tar, and in substitutes of turpentine oil: Required are an "acid mixture" of 1 vol. fuming and 3 vol. concentrated sulphuric acid (1,84); further, concentrated sulphuric acid (1,84), and a flask with a graduated neck. To 20 cc. of the acid mixture, 10 cc. of the substance under examination are added, with shaking, and, if necessary, cooling. After thorough mixing the flask is filled up with concentrated sulphuric acid, and after 2 to 3 hours the figures are read off the scale. An admixture of 30% or more petroleum hydrocarbons can then be detected, but if less has been added, more time must elapse before the reading off. The portion floating on the top, i. e. the one not absorbed by the acid, is estimated refractometrically according to Utz. But as it has been found that about 0,9 cc. of every 10 cc. pure turpentine oil are separated off in the treatment as a portion insoluble in the acid, 10 cc. of a turpentine oil containing 10% benzene or similar substance, should separate off

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1) Report April **1906**, 66.
2) Zeitschr. f. öff. Chemie **11** (1905), 429.
3) Pharm. Ztg. **51** (1906), 251.
4) ibidem 265.
5) Chem.-Ztg. **30** (1906), 633.

0,81 + 1 cc. = 1,81 cc., and 10 cc. of an oil containing 30 % benzene, 3,63 cc. This surplus however only applies to oils containing not more than 20 % benzene; oils with more than 50 % benzene even show a considerable deficiency. The author has drawn up the following figures: —

When	about	1,25	cc.	are	separated	off,	about	5 %	by	vol. adulteration
„	„	1,70	„	„	„	„	„	10 %	„	„ „
„	„	2,00	„	„	„	„	„	15 %	„	„ „
„	„	2,50	„	„	„	„	„	20 %	„	„ „
„	„	2,80	„	„	„	„	„	25 %	„	„ „
„	„	3,35	„	„	„	„	„	30 %	„	„ „
„	„	3,75	„	„	„	„	„	35 %	„	„ „
„	„	4,15	„	„	„	„	„	40 %	„	„ „
„	„	4,50	„	„	„	„	„	45 %	„	„ „

For the quantitative estimation of benzene in turpentine oils, etc. Böhme prefers Schreiber and Zetzsche's[1]) method, according to which for a mixture of equal parts by volume of turpentine oil and pure benzene, the bromine number 1,115 (g. Br per 1 cc. turpentine oil) was found. The bromine numbers of pure turpentine oils are on the average 2,20; only very old turpentine oil whose bromine number lies below 2,0, will give incorrect results.

With regard to these statements by Böhme, H. Herzfeld[2]) remarks that he can confirm the errors of the method in the case of a large admixture of benzene, but that, even when small quantities are added, he obtains unsatisfactory results. In the last-named cases he fractionates the substance and examines the individual fractions. The residue remaining behind in the treatment with sulphuric acid is further examined by Herzfeld in doubtful cases, after refracto-metric examination with fuming nitric acid, especially in the presence of resin oils.

In his studies on the use of dimethyl sulphate for the detection and the estimation of tar oils in mixtures with resin oil and mineral oil, E. Valenta[3]) has also observed the behaviour of dimethyl sulphate towards fatty oils, turpentine oil, and pinolin. Pinolin and turpentine oil, when shaken with equal parts of dimethyl sulphate, cause an increase in the volume of the layer of dimethyl sulphate, as about 30 % of the above-named substances are dissolved. Pinolin imparts an orange colour to the mixture; pure turpentine oil does not colour it, but a mixture of turpentine oil and dimethyl sulphate causes a large increase in the temperature, whilst pinolin with dimethyl sulphate produces only a scarcely perceptible rise in the temperature. The author believes that these reactions can be employed with advantage in the testing of turpentine oil for an admixture of pinolin.

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1) Chem.-Zeitg. **23** (1899), 676.
2) Chem.-Zeitg. **30** (1906), 697.
3) Ibidem 266.

A fatal case of poisoning owing to the inhalation of turpentine oil vapours is reported by A. Drescher[1]): a workman who varnished in a sugar works the interior of an iron vessel used for inverting sugar, died in consequence of the inhalation of turpentine vapours. Any other cause of death, such as suffocation by carbonic acid, heat stroke, genuine paralysis of the heart, poisoning by lead or arsenic, or intoxication by another poisonous or narcotic substance producing paralysis of the heart, is out of the question. As another workman had, previous to the one who died, been instructed to varnish the vessel, but had become so unwell, owing the the vapours of the varnish, that he was compelled to give up the work, the air in the vessel (which had a cubical content of only 132 cub. ft.) must have been so saturated with turpentine oil vapours, that the second workman who had already become unwell but had in spite of this resumed the work, died of the excessive inhalation of the vapour. — This would be the first fatal case of turpentine oil poisoning known, assuming of course that the varnish contained pure turpentine oil. But the death of the man may possibly be attributed to some other constituent of the varnish.

Oil of Umbellularia californica. As already reported by us on a previous occasion[2]), Power and Lees had made a thorough study of the oil of *Umbellularia californica* Nuttall, and they had then already succeeded in isolating a fraction which consisted chiefly of a ketone $C_{10}H_{14}O$ to which they gave the name umbellulone, and about which further details have also been given by us. In a publication by F. Tutin[3]) now before us, some derivatives of umbellulone and above all its constitution are discussed. On oxidation, umbellulone yields a saturated keto acid $C_9H_{14}O_3$, m. p. 102°, umbellulonic acid, which on distillation under suitable conditions is converted partly into the already described unsaturated lactone $C_9H_{12}O_2$, b. p. 218 to 221°, which on hydrolysis again results in umbellulonic acid, and with loss of water is formed from the enol-modification of the keto acid. On oxidation the lactone yields a remarkably stable polymethylene dicarboxylic acid, umbellularic acid $C_8H_{12}O_4$, m. p. 120 to 121°, which is not attacked even when boiled for ten hours with fuming nitric acid. When brominated, umbellulone yielded, in addition to the solid dibromide of the m. p. 119°, the liquid monobromo umbellulone (b. p. 140° at 20 mm. pressure), and also a fraction boiling at 130° (20 mm. pressure), which on distillation over sodium yielded p-cymene. This shows that the umbellulone molecule is capable of passing over into

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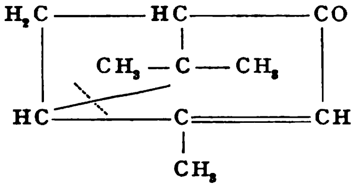
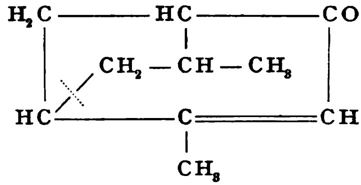
[1]) Concordia **13** (1906), 141.
[2]) Report October **1904**, 87.
[3]) Journ. chem. Soc. **89** (1906), 1104.

this hydrocarbon without any far-reaching change. The author suggests the following two possible formulæ: —

I.



II.



Both formulæ admit of the possibility of the formation of p-cymene, owing to the bridge-rupture by absorption of hydrogen at the spot indicated by the dotted line. Formula I represents a keto pinene, yielding on oxidation a dimethyltetramethylene dicarboxylic acid which should be identical or stereo-isomeric with norpinic acid formed by oxidation of pinene. But this appears to be as little the case, as that umbellulonic acid is stereo-isomeric with pinonic acid.

For this reason formula II corresponds much better with the construction of umbellulone, and according to this umbellularic acid would then represent 1-methylpentamethylene-3,5-dicarboxylic acid. The reduction of umbellulone with sodium and absolute alcohol yielded a mixture of two compounds, which were identified as β-dihydro umbellulone $C_{10}H_{16}O$, b. p. 204 to 209°, with a pulegone-like odour and a semicarbazone of the m p. 155 to 156°, and as tetrahydro umbellulone, $C_{10}H_{18}O$, b. p. 197 to 198°, with a camphor-like odour, and a semicarbazone of the m. p. 148°.

Verbena Oil. From the last Report of Roure-Bertrand Fils[1]) we abstract the following communication regarding *Verbena triphylla* L. and the oil obtained from it: The oil in question had been distilled during the flowering period of the plant; the roots (including the quantity of oil obtained by extraction of the distillation water) yielded 0,014 %, the stalks 0,007 % of oil.

The oil obtained from the leaves and inflorescences had the following composition: —

	Oil from the leaves	Oil from the inflorescences
yield in per cent. of the fresh plant	0,195	0,132
α_D	— 14° 16′	— 8° 24′
ester	3,5 %	3,2 %
combined alcohol	2,8 „	2,5 „
free alcohol	16,5 „	13,8 „
citral	35,4 „	29,6 „

[1]) Berichte, Roure-Bertrand Fils, April **1906**, 38; comp. also Reports October **1900**, 64; April **1903**, 76; Gildemeister and Hoffmann, The Volatile Oils, p. 593.

Ester and alcohol were not determined in the oil itself, but after treatment of the latter with neutral sodium sulphite solution and sodium bicarbonate in a special sample which had thereby been freed from citral. The figures obtained with the use of oil free from aldehyde were then calculated for the total oil.

Wormwood Oil. According to the chemical examinations[1]) made at the time in our New York laboratory, normal wormwood oil contains thujone, thujyl alcohol (free and as ester), phellandrene, pinene (?), cadinene, and a blue oil of unknown composition; thujone forms the principal constituent. Some wormwood oils, however, originating from the South of France behaved quite differently[2]). Of oil from wild wormwood Roure-Bertrand Fils examined two self-distilled samples, which originated from the mountains near Caussols (Alpes Maritimes) — one sample dating from 1900, the other from 1905.
The analysis gave the following results: —

	1900	1905
ester	9,0 %	5,5 %
combined alcohol	7,0 %	4,3 %
free alcohol . .	71,9 %	76,3 %
thujone . . .	8,4 %	3,0 %

These oils consequently contained only small quantities thujone; their principal constituent was thujyl alcohol. An oil which originated from plants sown in Grasse, and had also been distilled by the above-named firm, had the following composition: ester 35,6 %, combined alcohol 27,9 %, free alcohol 12,3 %, thujone 7,6 %. In this oil the chief constituent was therefore also thujyl alcohol, but it contained considerably more combined alcohol than the oil obtained from the plants growing wild.

Wormseed Oil, American. From a reprint from the "Medizinische Klinik" we abstract a communication made by H. Brüning[3]). The American wormseed oil, which in America is at the present day still used with good results as officinal anthelmintic, has here, strange to say, fallen entirely into oblivion. A pharmacological study by the author, at whose disposal we had placed the material for examination, had the result that live ascarides were in a short time destroyed in water or a solution of common salt or Ringer's solution at 38° C., with which the oil had been mixed, whilst the control parasites for a long time continued to move about. Even with solutions of 1 in 5000

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[1]) Report April **1897**, 47; comp. also Gildemeister and Hoffmann, The Volatile Oils, p. 685; further Charabot, Bull. Soc. chim. III. **23** (1900), 474.

[2]) Berichte, Roure-Bertrand Fils, April **1906**, 36.

[3]) H. Brüning, Die Behandlung der Askaridiasis. Reprint from the "Medizinische Klinik", **1906**, No. 29.

a paralysing, narcotic effect occurred within two hours, but when such ascarides were transferred to non-poisonous liquids they recovered their mobility in a short time. The same results were obtained with the principal constituent of the oil which we isolated a short time ago and whose formula we approximated as $C_{10}H_{16}O_2$. This body also appears to be the active constituent of wormseed oil, for its action was even much more powerful than that of the oil itself. According to his very extensive experimental studies, and a series of successfully accomplished worm-cures with patients, Brüning considers American wormseed oil an anthelmintic which has an action equal if not superior to that of santonin, and he intends using the oil and also the active constituent which we isolated from it, in experiments with other entozoa. The remedy is taken without any admixture, and not unwillingly, in emulsions, according to the following recipes: Ol. chenopodii anthelmint., Gum. arab. subtill. pulv. $\widehat{aa}$ 5,0 g., Aqu. dest., Sir. aurantior. $\widehat{aa}$ 45,0 g., or Ol. chenopodii anthelmint. 10,0 g., Vitellum ovi unius, Ol. amygdal., Gum. arab. pulv. $\widehat{aa}$ 10,0 g, Aqu. dest. ad 200,0 g.

Ylang Ylang Oil "Sartorius". In spite of the fact that we had to increase the price in the spring, owing to the advance in the prices of blossoms in Manila, the demand was exceptionally brisk, so much so that we could scarcely keep a stock of a few cases. This article is greatly appreciated especially by our clients in Paris.

New essential oils.

Two oils which had not been produced up to the present were sent to us for approval by the *Syndicat du Géranium Bourbon.* They are the oils from *Evodia simplex* Cordem., and from *Pilea* spec. nov. Both plants are indigenous to Réunion and grow there in the wild state.

Oil of Evodia simplex. This plant belonging to the family *Rutaceae* is closely allied to *Toddalia aculeata* Pers., which has essential oil[1]) both in the leaves and in the bark of the roots. The yellow-green, mobile oil has a pleasant, not obtrusive odour. The fact that the oil strongly reminds of Réunion geranium oil, is, according to the manufacturer, due to the use of stills employed in the geranium oil production. d_{15° 0,9737; $\alpha_D - 13^\circ 4'$; acid no. 2,1; ester no. 16,4; ester no. after acetylation 63,3. The oil forms a clear solution in 0,9 vol. 80 per cent. alcohol, with a slight separation of paraffin, but does not completely dissolve in 10 vol. 70 per cent. alcohol. In a freezing mixture it becomes cloudy with separation of a very few

[1]) Gildemeister and Hoffmann, The Volatile Oils, p. 460.

colourless scales, but does not solidify. After it had been seen that up to about 190° (ordinary pressure) nothing distilled over, the oil was fractionated *in vacuo* (3 mm. pressure), when it boiled between 90 and 140°. The portion passing over on repeated distillation from 97 to 100° (2,5 mm. pressure) (d_{15° 1,006; α_D — 4°) had a pronounced odour of eugenol methyl ether. The further examination showed that this body was actually present. The oxidation of 6 g. of this oil with a solution of 18 g. permanganate in about 400 cc. water gave a fair yield of veratric acid, colourless thin small needles of the m. p. 177,5°. Repeated recrystallisation did not raise the melting point further.

From the last fraction of the oil a body crystallised out which after recrystallisation from 90 per cent. alcohol formed long colourless needles, which proved to be a paraffin by their difficult solubility in alcohol, and their indifference towards concentrated nitric acid. Its melting point lay between 80 and 81°.

Eugenol methyl ether and a paraffin melting at 80 to 81° have, therefore, been found by us in the oil of *Evodia simplex* Cordem.

Pilea Oil. The still unnamed species of *Pilea* from which this oil had been distilled belongs to the *Urticaceae*, a family whose members had not up to the present yielded an essential oil. The water-white very mobile oil had a turpentine-like but not disagreeable odour. d_{15° 0,8533; α_D + 33°53′; n_{D20° 1,46862; ester no. 5,1; ester no. after acetylation 24,2; soluble in about 5 and more vol. 90 per cent. alcohol, with slight turbidity. On fractional distillation the oil passed over at 748 mm. pressure as follows: 1) 158 to 159° 6%; 2) 159 to 160° 35%; 3) 160 to 161° 10%; 4) 161 to 161,5° 10%; 5) 161,5 to 163° 10%; 6) 163 to 165° 10%; 7) 165 to 168° 7%; 8) 168 to 174° 2%; 9) 174 to 194° 8%. Residue (yellow, decomposed) 2%.

The fractions 1 to 7 were again distilled, this time over sodium. The portion boiling between 157 and 158° (d_{15° 0,8545; α_D + 14°35′; n_{D20° 1,46684) served for the production of a nitrosochloride compound which, when brought into reaction with benzylamine, yielded the pinene nitrolbenzylamine melting at 122°. This fraction consequently contained pinene, although in small quantity — as must be assumed from the low yield. The higher fraction boiling at 158 to 159° no longer yielded a nitrosochloride. The attempt to detect camphene in the fraction of the b. p. 160°, by conversion into isobornyl acetate, gave no result, and for this reason it is still undecided what the bulk of pilea oil consists of.

Dittany Oil. A distillate which was sent to us under the name of "Essence de Dictame blanc ou Calament" from Oran (Algeria), corresponded in its properties fairly well with the calamintha oil (*Cala-*

mintha nepeta)[1] recently mentioned by us, but also resembled the oil of European pennyroyal. As we were interested in becoming acquainted with the plant from which the oil had been distilled, we obtained a few dried specimens and endeavoured to recognise them. Unfortunately the plants placed at our disposal were incomplete (the blossoms were missing), but in spite of this we believe that we are justified in identifying the plant as *Amaracus dictamnus* (L.) Benth. (*Origanum dictamnus* L., dittany), indigenous to Crete, and which for the rest is largely cultivated as an ornamental plant. Among the ancient Greeks and Romans the plant was renowned as a medicinal herb which was employed as an excitant and diaphoretic. It should not be confounded with *Dictamnus albus* L., an aromatic plant growing here which also yields an essential oil. — Our sample had a yellowish colour and a strong odour of pulegone. The constants were as follows: $d_{15°}$ 0,9331; $\alpha_D + 3°$; soluble in 2,7 vol. 70 per cent. alcohol with faint opalescence, which increases when more alcohol is added; soluble in 1,5 and more vol. 80 per cent. alcohol, when 14 vol. are added cloudiness occurs. The oil contained about 85 % pulegone with a rotatory power of $+ 20° 10'$; the pulegone was isolated by means of sodium sulphite solution.

Oil of Pastinaca roots. See under Pastinaca oil, p. 51.

New Pharmacopœias.

Of new pharmacopoeias, we have to mention the 4th edition of the Dutch and the 3rd edition of the Belgian. To the former we referred already in our last Report, but we found it then impossible to obtain a copy in good time, and we were therefore compelled to postpone the discussion until the present Report. In addition to the pharmacopœias mentioned above, the supplement to the 4th edition of the German Pharmacopœia published by the „Deutscher Apotheker-Verein“ has also appeared, whose articles as far as they are of interest to us shall be discussed here.

Dutch Pharmacopœia.

(Pharmacopœia Nederlandica ed. IV.)

Whilst the 3rd edition of the Dutch Pharmacopœia left much to be desired as to the description and testing of essential oils, the new edition shows an undeniable advance over the former. The particulars given are on the whole correct, and errors of any importance (which, however, it would have been easy to avoid) there

[1]) Report April **1903**, 50. Comp. also the present Report p. 14.

are few. The number of officinal oils has been augmented with several, and in addition to anise oil and clove oil, their principal constituents anethol and eugenol have now also been included.

The data with regard to solubility and specific gravity are given for a temperature of 15°, and in the latter case are compared with water at + 4°. We have convinced ourselves by comparative estimations that the differences between the specific gravities as compared with water at + 15° and at + 4° are so slight that for practical purposes they can be neglected, and the specific gravities given in the pharmacopoeia can therefore be taken as if they were based upon that of water at + 15°.

Spiritus fortior, with 95 per cent. (by volume) alcohol;
Spiritus, with 90 per cent. (by volume) alcohol;
Spiritus dilutus, with 70 per cent. (by volume) alcohol.

Anethol (*Anetholum*). White crystalline mass; $d_{25°}$ 0,984 to 0,986; $\alpha_D \pm 0°$; m. p. 21°[1]; b. p. about 235°; at 20° soluble in 2 vol. spiritus.[2]

[1]) The m. p. of pure anethol lies between 22 and 23°, the sol. p. between 21 and 22°.

[2]) For dissolving 1 vol. anethol, 2 to 3 vol. 90 per cent. alcohol are required.

Anise Oil (*Oleum anisi*). Colourless or yellowish; $d_{15°}$[1]) 0,980 to 0,990; sol. p. not below 14°; soluble at 20° in 2 vol. spiritus.[2])

[1]) It is desirable to determine the spec. gravity at 20°, as at 15° solidification of the anise oil may occur; the limits of value remain the same as at 15°.

[2]) Anise oil dissolves in 2 to 3 vol. 90 per cent. alcohol.

Cajeput Oil (*Oleum cajuputi*). Blueish green; $d_{15°}$ 0,920[1]) to 0,930; boiling temperature 155 to 180°; soluble in every proportion in alcohol; when shaken with dilute acetic acid the colour of cajeput oil changes to yellow, in the acid aqueous liquid traces of copper can be detected; cineol reaction with iodine, and test for fatty oil.

[1]) The spec. gravity is frequently also slightly lower: 0,919.

Cherry laurel Oil (*Oleum laurocerasi*). Yellowish; $d_{15°}$ 1,060 to 1,067[1]); soluble in 2 vol. spiritus dilutus; if 1 cc. oil is heated with shaking on a water bath with 10 cc. of a 30 per cent. sodium bisulphite solution, the oil should completely dissolve[2]); hydrocyanic acid reaction.

[1]) The lower limit of value is given too high and should be 1,050, and if the oil has a high content of hydrocyanic acid, the upper limit may be exceeded.

[2]) In the concentrated sodium bisulphite solution the bisulphite compound dissolves with great difficulty; complete solution only occurs when about an equal volume water is added.

Cinnamon Oil, Ceylon (*Oleum cinnamomi*). When freshly prepared yellow, becoming in course of time yellow-red or brownish,

when the oil also becomes viscid; $d_{15°}$ 1,025 to 1,040; the bulk of the oil boils at about 250°; the distillation-residue may amount to at most 10%; soluble in every proportion in spiritus, and in 3 vol. spiritus dilutus; the spirituous solution has an acid reaction; content of cinnamic aldehyde 55 to 75%; nitric acid test; test for eugenol, alcohol, and fatty oil.

Clove Oil (*Oleum caryophyllorum*). When freshly prepared almost colourless, subsequently yellowish, finally red-brown: $d_{15°}$ not below 1,05; soluble in every proportion in spiritus and in 2 vol. spiritus dilutus; identity reactions.

Eugenol (***Eugenolum***). When freshly prepared almost colourless, subsequently yellowish, finally red-brown; $d_{15°}$ 1,072[1]) to 1,074; b.p. about 252°; soluble in every proportion in spiritus, ether, and glacial acetic acid, also in 2 vol. spiritus dilutus. Identity reactions, test for phenol.

[1]) Eugenol distilled *in vacuo* and absolutely free from water, is frequently somewhat lighter; we have recently observed in our own preparations down to 1,0713.

Fennel Oil (*Oleum foeniculi*). Almost colourless: $d_{15°}$ 0,965 to 0,980; α_D + 12 to + 24°; when cooling gradual solidification takes place with separation of anethol; a fennel oil which does not separate off at 0° crystals dissolving again completely at + 5°, must be rejected[1]); forms a clear solution with an equal vol. spiritus; on distillation at least half the fennel oil must pass over between 225 and 240°.

[1]) It would have been better if a definite solidification point had been substituted for these statements; this should not lie below + 4°. But it must be taken into consideration that solidification may have to be brought about by inoculation with a small crystal of anethol, as fennel oil can occasionally be cooled down considerably without solidifying; when the sol. p. is to be determined, the oil should be cooled to + 2 or + 3°.

Lavender Oil (*Oleum lavandulae*). Colourless or yellowish; $d_{15°}$ 0,880 to 0,890[1]); soluble in every proportion in spiritus, also in 3 vol. spiritus dilutus[2]); content of linalyl acetate at least 35%.

[1]) The upper limit of value is 0,895.
[2]) The solubility mentioned applies to an observation-temperature of 20°.

Lemon Oil (*Oleum citri*). Yellowish; $d_{15°}$ 0,850 to 0,860[1]); $\alpha_{D20°}$ + 58 to + 67°[2]): soluble in 6 vol. spiritus[3]); if 50% of the lemon oil are distilled off, the distillate must have a higher rotation than the original oil.

[1]) The spec. gravity of lemon oil fluctuates between 0,857 and 0,861.
[2]) The highest permissible rotation is + 65°.
[3]) The vegetable wax-like constituents contained in lemon oil generally prevent from a clear solution.

Mace Oil (*Oleum macidis*). Colourless or faintly yellowish; $d_{15°}$ 0,900 to 0,920[1]); soluble in 3 vol. spiritus; on distillation at least

half should pass over between 110 and 130°; of the balance part should pass over between 130 and 150°, and the remainder above 200° [2]).

[1]) The limits should be made wider: 0,890 to 0,930.

[2]) The statements on the behaviour of mace oil on boiling are quite wrong. The oil boils chiefly (about 75 %) between 165 and 200°, the balance between 200 and 280°. Th. Hoogenboom has also recently called attention to this, and his statements agree on the whole with ours. Comp. Pharm. Weekblad **43** (1906), 743.

Menthol (*Mentholum*). Colourless, hexagonal prisms; soluble in 0,2 parts spiritus, readily in chloroform and ether; m. p. 43°; b. p. 216°; when triturated with camphor, thymol or chloral hydrate it liquefies; if a solution of 1 g. menthol in 5 cc. spiritus is mixed with 5 cc. water, the mixture must have a neutral reaction; menthol must be completely volatile at the temperature of the water bath.

Methyl Ester of Salicylic Acid (*Salicylas methylicus*). Colourless, completely volatile; neutral reaction; d_{15° 1,176 [1]); b. p. 223 to 224°; soluble in every proportion in spiritus; identity reactions.

[1]) The spec. gravity indicated is wrong; it should be 1,185 to 1,190.

Mustard Oil (*Oleum sinapis*). Colourless or yellowish; d_{15° 1,018 [1]) to 1,025; soluble in every proportion in spiritus; sulphuric acid test; thiosinamine test.

[1]) We have observed in our own distillates down to 1,014.

Orange Oil, bitter (*Oleum aurantiorum*). Yellowish; d_{15° 0,850 to 0,870 [1]); on distillation the oil should almost completely pass over between 175 and 180°; soluble in 7 vol. spiritus [2]).

[1]) The upper limit of value is given too high; we have never observed in pure oils above 0,860.

[2]) The solutions are not always clear, owing to the presence of wax-like constituents.

Peppermint Oil (*Oleum menthae piperitae*). Colourless or yellowish; d_{15° 0,900 to 0,920 [1]); soluble in every porportion in spiritus and in 5 vol. spiritus dilutus, in the last-named case possibly with faint opalescence; content of total menthol at least 51,68 %; colour reaction with glacial acetic and nitric acids.

[1]) According to the specific gravity both English and American oils are admitted.

Rose Oil (*Oleum rosarum*). At 20° yellowish to greenish liquid; d_{30° 0,850 to 0,860 [1]); when cooled solidification takes finally place with separation of small crystals; when diluted with 10 times the vol. spiritus, rose oil gives a mixture clouded by flaky separations, when heated to a little above 30°, the flakes are partly dissolved, and partly float as oil drops on the surface of the liquid.

[1]) The limits of value at 30° are 0,849 and 0,862.

Rosemary Oil (*Oleum rosmarini*). Colourless or greenish yellow; d_{15° 0,900 to 0,920; α_D not above + 15° [1]); α_D of the first 10 % of the distillate also to the right; soluble in 0,5 vol. spiritus; on

distillation more than half the oil must pass over between 165 and 175°, the remainder, with the exception of a slight resinous residue, between 190 and 205°; from the latter distillate camphor crystals frequently separate off when it is cooled.

[1]) The pharmacopoeia specifies the above rotation for a tube of 200 mm., but this is incorrect and is clearly due to an oversight. Pure rosemary oil rotates in a 100 mm. tube up to + 15°.

Sandalwood Oil, East Indian (*Oleum santali*). Yellowish; $d_{15°}$ 0,975 to 0,985; α_D — 17[1]) to — 20°; soluble in 2 vol. spiritus and in 5 vol. spiritus dilutus[2]); santalol-content at least 92,5%[3]); sandal oil must not contain portions boiling below 290°, the bulk of the oil passes over above 300°.

[1]) Sometimes, although rarely, these oils rotate somewhat lower. Comp. Report October **1905**, 64.

[2]) The statements on the solubility in spiritus dilutus apply to 20°; at an observation temperature of 15° most sandal oils would not pass the test.

[3]) The pharmacopœia bases the calculation on the old formula $C_{15}H_{26}O$. Calculated for the formula $C_{15}H_{24}O$ which according to our present knowledge is more correct, the lowest content of santalol is 91,7%.

Terpin Hydrate (*Hydras terpini*). Colourless crystals; m. p. 116°; soluble in 230 parts water and 12,8 parts spiritus, the solutions are neutral; when dried at 100° it is converted into terpin which melts at 102°; 1 g. should leave behind not more than 3 mg. ashes; identity reactions.

Thymol (*Thymolum*). Colourless crystals; m. p. 49 to 50°[1]); b. p. 232 to 234°; solid thymol sinks in water, liquid thymol floats on it; soluble in 1175 parts water, in 0,4 parts spiritus, readily in chloroform and in ether, the solutions must have a neutral reaction; 0,1 g. thymol must volatilise on the water-bath without weighable residue; identity reactions and test for phenol.

[1]) Thymol melts between 50 and 51°.

Turpentine Oil, American (*Oleum terebinthinae*). Almost colourless, not fluorescent; $d_{15°}$ 0,860 to 0,890; α_D — 3 to + 15°; mostly between + 10 and + 14°; at least 90% of the oil must pass over between 155 and 165°; soluble in 8 vol. spiritus.

Turpentine Oil, rectified (*Oleum terebinthinae depuratum*). Colourless; $d_{15°}$ 0,860 to 0,872; boiling temperature 155 to 165°, soluble in an equal vol. glacial acetic acid and in 6 vol. spiritus, the spirituous solution must not redden litmus paper.

Belgian Pharmacopœia.

(Pharmacopœia Belgica ed. III.)

The articles of the new Belgian Pharmacopœia which are of interest to us have already been discussed in our October Report **1903** (p. 71) when the draft pharmacopœia had appeared in the "Annales de

Pharmacie" (9 [1903], 193). It gives us great pleasure to be able to state that our suggestions made at the time have throughout received consideration, so that now we have little to discuss, and can on the whole limit ourselves to a recital of the requirements specified by the pharmacopœia. The procedure of the Belgian Pharmacopœia Committee, to submit their draft first to public discussion, appears to us to be well worthy of imitation, for only in this manner is it possible to avoid incorrect requirements or such as cannot be fulfilled, which are unfortunately up to the present met with in all pharmacopœias, and which continually give rise to disagreeable discussions between the reviser, the chemists, and the manufacturers.

The strength of the alcohol required is between 94,09 and 95 per cent. by volume.

Anethol (*Anetholum, essentia anisi*)[1]. White crystalline leaflets; m. p. 22°; b. p. 232 to 234°; d_{25° 0,984 to 0,986; $\alpha_D \pm 0^\circ$; sparingly soluble in water, soluble in alcohol.

[1]) It would have been better to omit the designation "*essentia anisi*" for anethol, even if synonymous, as anise oil and anethol are not identical; in its place, a note at the end of the article might have mentioned that when anise oil is prescribed anethol should be substituted. The same applies to benzaldehyde, eugenol, eucalyptol, methyl ester of salicylic acid, and thymol.

Balm Oil (*Essentia melissae*)[1]. Colourless or yellowish.

[1]) Compare here what is said under the discussion of the Supplement to the German Pharmacopœia, page 93.

Benzaldehyde (*Aldehydum benzoicum, essentia amygdalae amarae, essentia laurocerasi*)[1]. Obtained from the oils of bitter almonds or cherry laurel, or synthetically; colourless; d_{15° 1,050 to 1,055; $\alpha_D \pm 0^\circ$; b. p. 179°; sparingly soluble in water, soluble in every proportion in alcohol. The freshly prepared aldehyde does not redden litmus paper, but in a short time becomes acid when air is admitted. If 5 g. benzaldehyde are shaken with 45 g. of a saturated solution of sodium bisulphite, and the mixture after adding 60 g. water is heated on the water bath, a clear solution must result. Test for the absence of hydrocyanic acid and nitrobenzene.

[1]) Comp. note under anethol.

Bergamot Oil (*Essentia bergamotti*). Brownish yellow or greenish; d_{15° 0,88 to 0,89; soluble in spiritus; residue on evaporation about 5 to 6 %; content of linalyl acetate (determined after neutralising the free acid) 30 to 45 %.

Camphor (*Camphora*). White, transparent mass; lighter than water; m. p. 175°; volatile without weighable residue; very sparingly soluble in water, readily in alcohol, ether, chloroform, fat' essential oils.

Cassia Oil (*Essentia cinnamomi*). Yellow or brownish; d_{15° 1,055 to 1,070; aldehyde-content at least 70 %[1]); residue on evaporation not above 8 %[2]); soluble in 1 to 2 parts 80 per cent. alcohol[3]); nitric acid test; ferric chloride reation.

In addition to cassia oil, pure cinnamic aldehyde and Ceylon cinnamon oil are also admitted.[4])

[1]) The aldehyde-content of good cassia oils is at least 75 %.

[2]) In view of the difficulty of volatilising cinnamic aldehyde, the cassia oils will answer this requirement only in exceptional cases. We have in a pure oil determined the following values: residue on evaporation after 5 hours, 54,6 %, after 14 hours 28,9 %, after 24 hours 19,0 %. For this reason the above-mentioned requirement of the pharmacopœia only applies to the distillation-residue, for the determination of which see Gildemeister and Hoffmann, The Volatile Oils, p. 382.

[3]) The solution shows occasionally a faint opalescence.

[4]) For cinnamic aldehyde and Ceylon cinnamon oil we give here the properties:

Cinnamic aldehyde. Bright yellow: d_{15° 1,054 to 1,058; $\alpha_D \pm 0^\circ$; b. p. about 252°, with partial decomposition; solidifies when much reduced in temperature, and melts again at — 7,5°; soluble in about 2 vol. 70 per cent. alcohol; must be free from compounds containing chlorine.

Ceylon cinnamon oil. Bright yellow; d_{15° 1,023 to 1,040; α_D slightly to the left, to — 1°; aldehyde-content between 65 and 76°; soluble in 2 to 3 and more vol. 70 per cent. alcohol.

Chamomile Oil, Roman (*Essentia chamomillae*). Blue, subsequently green, finally yellow-brown; d_{15° 0,905 to 0,915; sap. no. 250 to 300; soluble in 2 vol. 80 per cent. alcohol.

Eucalyptol (*Eucalyptolum, essentia eucalypti*)[1]). Colourless; d_{15° 0,928 to 0,930; $\alpha_D \pm 0^\circ$; b. p. 176 to 177°; almost insoluble in water, readily soluble in alcohol, ether, chloroform and fatty oils; makes a clear solution with an equal vol. *Paraffinum liquidum*; in a freezing mixture eucalyptol must solidify at —1° into long colourless needles[2]); volatile on the water bath without residue; identity reaction with bromine.

[1]) Comp. note under anethol.

[2]) Solidification must if necessary be started by rubbing a glass rod on the side of the vessel.

Eugenol (*Eugenolum, essence de girofle*)[1]). Colourless or yellowish, becoming brown on exposure to the air; d_{15° 1,072[2]) to 1,074; b. p. 251 to 253; sparingly soluble in water, completely in alcohol, ether, and glacial acetic acid; identity reactions and test for phenol.

[1]) Comp. note under anethol.

[2]) Comp. note p. 86 in the discussion of the Dutch Pharmacopœia under eugenol.

Fennel Oil (*Essentia foeniculi*). Colourless or yellowish; d_{15° 0,965 to 0,975[1]); soluble in an equal vol. alcohol; at 0° crystals of anethol separate off, which dissolve again at + 5°[2]).

[1]) Fennel oil is often a little heavier, up to 0,977.
[2]) Comp. the corresponding note in the discussion of the Dutch Pharmacopœia under fennel oil, p. 86.

Lavender Oil (*Essentia lavandulae*). Colourless, yellowish, or greenish yellow; d_{15° 0,885 to 0,895; soluble in 3 parts 70 per cent. alcohol; content of linalyl acetate (determined after neutralising the free acid) at least 29,4 %.

Lemon Oil (*Essentia citri*). Bright yellow; d_{15° 0,858[1]) to 0,861; α_D + 58 to + 65°; soluble in 5 parts spiritus, the solution may be opalescent.

[1]) Sometimes good oils occur with a spec. grav. of 0,857.

Menthol (*Mentholum*). Needle-shaped colourless crystals; m. p. 42 to 43°; b. p. 212°; almost insoluble in water, readily soluble in alcohol, ether, and chloroform; test for thymol; 0,1 g. menthol must be completely volatile at the temperature of the water bath.

Methyl Ester of Salicylic Acid (*Methylum salicylicum*, *essence de wintergreen*)[1]). Colourless; d_{15° 1,18 to 1,19; b. p. 220°; sap. no. not below 360; sparingly soluble in water, soluble in alcohol and ether; ferric chloride reaction.

[1]) Comp. note under anethol.

Mustard Oil (*Essentia sinapis*). Colourless or yellowish; d_{15° 1,016 to 1,025; b. p. about 149°; very sparingly soluble in water, readily in alcohol, ether, and carbon disulphide; content of isothiocyanallyl at least 94,2 %[1]); sulphuric acid test; test with ferric chloride.

[1]) The pharmacopœia specifies the determination in the same manner as the German Pharmacopœia IV, but if carried out strictly the values obtained by it are too low. Comp. Report April **1906**, 45. Determinations carried out by us with our own distillates gave in the case of natural mustard oil a content of about 94 %, and with artificial oil about 98 % isothiocyanallyl.

Nutmeg Oil (*Essentia myristicae*). Colourless or yellowish; d_{15° 0,865 to 0,920[1]); soluble in 3 parts alcohol.

[1]) The upper limit of value is given too low, and should be 0,930.

Orange blossom Oil (*Essentia aurantii citri florum*). Yellowish, becoming brown in daylight; d_{15° 0,870 to 0,880; sap. no. 20 to 55; soluble in 1,5 to 2 vol. 80 per cent. alcohol with blue-violet fluorescence; when more alcohol is added the solution becomes cloudy.

Orange Oil, bitter (*Essentia aurantiorum corticum*). Yellow or brownish; d_{15° 0,848 to 0,852[1]); forms a cloudy solution with alcohol.

[1]) The spec. grav. quoted has reference to the oil of the sweet orange; oil of bitter orange has d_{15° 0,854 to 0,857.

Peppermint Oil (*Essentia menthae*). Colourless or yellowish; d_{15° 0,900 to 0,920[1]); soluble in an equal vol. alcohol; colour-reaction.

[1]) Comp. note in the Dutch Pharmacopœia under peppermint oil.

Rose Oil (*Essentia rosae*). Bright yellow; soluble in an equal vol. chloroform; the oil is again partly precipitated from the solution by the addition of alcohol. When the liquid oil is cooled to 18 to 21°, crystals of needle- or leaflet-shaped separate off from it.

Rosemary Oil (*Essentia rorismarini*). Colourless or yellowish; d_{15° 0,900 to 0,920; soluble in half its weight of alcohol.

Rue Oil (*Essentia rutae*). Colourless or yellowish; d_{15° 0,833 to 0,840; soluble in 2 to 3 parts 70 per cent. alcohol; when cooled it solidifies at + 8 or + 10°.

Sandalwood Oil, East Indian (*Essentia santali*). Bright yellow; d_{15° 0,975 to 0,985; b. p. 275 to 295°[1]); santalol-content at least 90 %[2]); soluble in 5 parts 70 per cent. alcohol.[3])

1) Comp. Gildemeister and Hoffmann, The Volatile Oils, p. 340, note 2.
2) We wish to point out specially that the santalol-content is calculated on the formula $C_{15}H_{24}O$.
3) The solubility mentioned applies to a temperature of 20°.

Savin Oil (*Essentia sabinae*). Colourless or yellowish; d_{15° 0,910 to 0,930; soluble in half its weight of alcohol.

Thymol (*Thymolum, essence de thym*)[1]). Colourless, transparent crystals; m. p. 50 to 51°; b. p. 230°; very slightly soluble in water, readily in alcohol, ether, chloroform and the aqueous solutions of caustic alkalies; 0,1 g. thymol must volatilise without residue at the temperature of the water-bath; identity reactions and test for phenol.

1) Comp. note under anethol.

Turpentine Oil, rectified (*Essentia terebinthinae*). Colourless; d_{15° 0,860 to 0,870; b. p. 155 to 162°; soluble in 12 parts alcohol; the alcoholic solution must not redden litmus paper moistened with water.

Wild Thyme Oil (*Essentia serpylli*). Colourless or yellowish; d_{15° 0,890 to 0,920.

Supplement to the Pharmacopœia of the German Empire.

(3rd. Edition.)

The fact that the supplement has acquired a permanent place alongside the pharmacopœia induces us to discuss here also the articles referring to essential oils, as several of the statements made require to be corrected or supplemented, as they might otherwise lead to a wrong opinion on various oils.

The strengths of the alcohols are the same as in the German Pharmacopœia IV, viz., spiritus with 90 to 91,2 per cent. by volume, and spiritus dilutus with 68 to 69 per cent. by volume.

Almond oil, bitter (*Oleum amygdalarum aethereum*). Colourless or yellowish; d_{15° 1,052 to 1,058[1]); soluble in an equal part of alcohol, and also in about 200 parts of water. Test for hydrocyanic acid, and for the absence of nitrobenzene and chlorinated products.[2])

[1]) The limits of value are taken too narrow, the specific gravity lies between 1,045 and 1,070 (15°).
[2]) With regard to the test for chlorinated compounds, comp. Report October **1904**, 8.

Amber Oil, rect. (*Oleum succini*). Bright yellow[1]); mobile; d_{15° 0,925 to 0,930[2]); soluble in 4 to 4,5 vol. 95 per cent. alcohol.

[1]) The oil is also frequently brownish yellow or olive-coloured.
[2]) We have in recent times observed in our own distillates even higher specific gravities (up to 0,935).

Balm Oil (*Oleum melissae*)[1]). Colourless or pale yellowish; feeble acid reaction; d_{15° 0,875 to 0,920; soluble in 2 to 3 parts alcohol.

[1]) Balm oil is not a commercial product; the commercial oil is not a pure distillate of melissa, but either a lemon or citronella oil distilled over melissa herb, or only a fractionated citronella oil.

Bergamot Oil (*Oleum bergamottae*). Greenish-yellow to green[1]); d_{15° 0,883[2]) to 0,886; soluble in every proportion in alcohol[3]).

[1]) Bergamot oil has also sometimes the colour of honey.
[2]) The lower limit of value should be reduced to 0,881.
[3]) For dissolving 1 vol. bergamot oil, up to $^1/_2$ vol. 90 per cent. alcohol is often required.

Cajeput Oil (*Oleum cajeputi*). Colourless to yellowish[1]); d_{15° 0,915 to 0,930; soluble in every proportion in alcohol; cineol reaction with iodine, and test for absence of copper.

[1]) From this as well as from the copper test, it is clear that the rectified oil is required, which, however, should be described correctly as *ol. cajeputi rectificatum*; the ordinary commercial product has a green colour owing to traces of copper.

Chamomile Oil (*Oleum chamomillae aethereum*). Fairly viscid, at low temperature almost like butter; dark blue[1]); d_{15° 0,930[2]) to 0,940; soluble in 8 to 10 parts alcohol[3]); the solution does not redden blue litmus paper.

[1]) Under the influence of light and air the colour changes gradually into green to brown.
[2]) The lower limit of value is given too high, and should be 0,925.
[3]) Owing to its high content of paraffin the oil gives only cloudy mixtures with 90 per cent. alcohol.

Cinnamon Oil (*Oleum cinnamomi zeylanici*). Yellow; somewhat viscid; d_{15° 1,024 to 1,040; soluble in every proportion in alcohol.

Eucalyptol (*Oleum eucalypti*)[1]). Colourless: d_{15° 0,930[2]); b. p. 176 to 177°; when cooled considerably, solidifying into colourless crystals.

which melt again at $-1°$; cineol reaction with bromine, test for absence of water.

[1]) Comp. in the present Report the note under anethol (Belgian Pharmacopoeia).

[2]) The specific gravity of eucalyptol lies between 0,928 and 0,930 (15°).

Orange Oil, bitter (*Oleum aurantii corticis*). Yellowish[1]); $d_{15°}$ 0,848 to 0,852[2]); soluble in 5 to 10 parts alcohol[3]).

[1]) The oil has a brownish yellow colour.

[2]) The spec. gravity mentioned applies to sweet orange oil; the oil of bitter orange has the specific gravity $d_{15°}$ 0,854 to 0,857.

[3]) Owing to the content of wax-like constituents, the oil generally forms only a cloudy solution with 90 per cent. alcohol.

Orange blossoms Oil (*Oleum aurantii florum*). Colourless[1]) to brownish; $d_{15°}$ 0,870 to 0,880; soluble in 1 to 2 parts alcohol; the solution has a blue-violet fluorescence.

[1]) Oil of orange blossoms is never colourless, even the fresh distillate is always yellowish.

Origanum Oil, Cretian (*Oleum origani cretici*). Somewhat viscid; yellow to red-brown; $d_{15°}$ 0,920 to 0,980; soluble in 3 parts dilute alcohol, the solution is coloured violet or (more rarely) green by ferric chloride. 2 vol. oil of Cretian origanum must make a clear solution with 1 vol. soda liquor.

Parsley seed Oil (*Oleum petroselini*). Yellowish to pale greenish somewhat viscid; when shaken with water, or in the cold, a solid crystalline body[1]) is sometimes separated off; $d_{15°}$ 1,050 to 1,10.

[1]) This body is apiol.

Pine Needle Oil from Pinus Pumilio (*Oleum pini pumilionis*). Colourless to bright yellow; $d_{15°}$ 0,865 to 0,875[1]); makes a clear or slightly cloudy solution with 5 to 7 vol. alcohol.

[1]) Comp. the present Report, p. 62.

Pine Needle Oil from Pinus Silvestris (*Oleum pini silvestris*)[1]). Colourless to yellow-greenish; $d_{15°}$ 0,880; soluble in 5 to 6 parts alcohol.

[1]) As the oil distilled from the needles of *Pinus silvestris* L. is not at all a commercial article, and as moreover the name *Oleum pini silvestris* is an old but incorrect designation of "*templin oil*" (oil from the cones of *Abies alba*), it would have been better to have included *Oleum templini*, whose spec. grav. lies between 0,85 and 0,87 (15°).

Rue Oil (*Oleum rutae*). Colourless or yellowish; $d_{15°}$ 0,833 to 0,840; solidifies at about $+8°$; soluble in an equal vol. alcohol.

Sage Oil (*Oleum salviae*). Mobile; yellowish; $d_{15°}$ 0,915 to 0,925; soluble in every proportion in alcohol.

Sassafras Oil (*Oleum sassafras*). Mobile; yellowish to reddish yellow; $d_{15°}$ 1,070 to 1,080; readily soluble in alcohol[1]).

[1]) Comp. Report April **1906**, 61.

Savin Oil (*Oleum sabinae*). Mobile when in fresh condition; colourless or yellowish, in course of time becoming dark and viscid; $d_{15°}$ 0,910 to 0,930; soluble in an equal volume alcohol.

Spearmint Oil (*Oleum menthae crispae*). Colourless, yellowish or greenish yellow; $d_{15°}$ 0,920 to 0,940; soluble in every proportion in alcohol[1]); does not decrepitate with iodine[2]).

[1]) The oil forms with 90 per cent. alcohol a solution which is clear only in the beginning; when more alcohol is added, opalescence occurs.
[2]) This reaction is valueless and superfluous.

Spike Oil (*Oleum spicae*). Colourless[1]) or green-yellowish; $d_{15°}$ 0,905 to 0,915; soluble in 1,7 to 2,6 parts dilute alcohol, clear or with slight turbidity[2]).

[1]) Spike oil is never colourless, but always yellowish.
[2]) Even a slight turbidity should disappear immediately if more alcohol is added, otherwise the oil is probably adulterated.

Star-anise Oil (*Oleum anisi stellati*). Colourless or yellowish; $d_{15°}$ 0,980 to 0,990; solidifies at about $+ 2°$[1]); soluble in alcohol[2]).

[1]) The sol. p. of pure star-anise oil lies above $+ 14°$; solidification must, if need be, be started by inoculation with a small crystal of anethol. It is surprising that such antiquated statements as the above continue to be found from time to time in books, although they have been disproved long since. Umney, as long ago as 1889, called attention to the incorrectness of the statement that star-anise oil solidifies at $+ 2°$, and we have also pointed it out repeatedly in our Reports.
[2]) Star-anise oil dissolves in 1,5 to 3 vol. 90 per cent. alcohol.

Tansy Oil (*Oleum tanaceti*). Yellow or greenish yellow, becomes brownish on exposure to the light; $d_{15°}$ 0,923 to 0,954; readily soluble in alcohol.

Valerian Oil (*Oleum valerianae*). Somewhat viscid[1]); brownish or greenish yellow; $d_{15°}$ 0,930 to 0,960; readily soluble in alcohol; the solution has an acid reaction. If 1 drop of the oil is dissolved in 20 drops carbon disulphide, shaken with 1 drop sulphuric acid, and then 1 drop nitric acid added, the carbon disulphide acquires a deep-blue or violet colour if shaking is continued[2]).

[1]) Valerian oil in fresh condition is mobile.
[2]) Such reactions are absolutely valueless for estimating essential oils.

Wild Thyme Oil (*Oleum serpylli*). Colourless to golden yellow; $d_{15°}$ 0,890 to 0,920; soluble in alcohol in every proportion.

Wintergreen Oil a) natural (*Oleum gaultheriae*)[1]). Colourless, yellowish or reddish; $d_{15°}$ 1,180 to 1,187; readily soluble in alcohol; identity reactions.

b) artificial (*Methylum salicylicum*). Colourless; $d_{15°}$ 1,1819[2]); b. p. 220°; readily soluble in alcohol; identity reaction with ferric chloride.

[1]) Natural oil of wintergreen is obtained from two different plants: *Gaultheria procumbens* L. and *Betula lenta* L. The two oils are of absolutely equal value.
[2]) The spec. grav. is incorrectly given, and should be $d_{15°}$ 1,185 to 1,190.

Wormwood Oil (*Oleum absinthii*). Dark green[1]); d_{15° 0,925[2]) to 0,955; soluble in 2 to 4 parts 80 per cent. alcohol[3]).

[1]) Wormwood oil often has a blue or brown colour.

[2]) 0,900 would be more correct as lower limit of value.

[3]) The dilute solution in 80 per cent. alcohol often shows opalescence or cloudiness, as a matter of fact many oils do not make clear solutions.

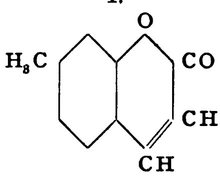
Chemical preparations and drugs.

Ambergris. The fine quality continues as before in great demand, and our stocks have meanwhile dwindled down considerably, while we have not been able to make up for it by procuring a corresponding quantity of equally good quality. To obtain this is to some extent a matter of chance.

Civet. Our well-assorted and large stock of pure original quality is probably unparalleled. In our purchases we are extremely particular, and the brisk demand which especially this important article enjoys from the side of the perfumery trade, may be a sufficient guarantee that our supplies meet the most subtile requirements.

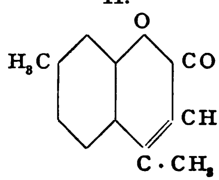
Coumarin. According to K. Fries and W. Klostermann[1]) the formation of coumarines from m-cresol passes off readily, whilst v. Pechmann's method for producing coumarin from phenol, o-, and p-cresol is not so easily accomplished. A work on this subject by Chuit and Bölsing to which we have already referred in our last Report[2]) induces the first-named authors to publish now a preliminary communication. From m-cresol they produced with malic acid, aceto-acetic ester, and methyl aceto-acetic ester the following compounds:

I.



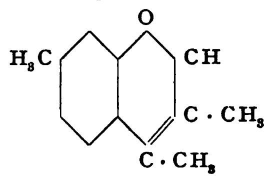
4-methyl coumarin

II.



2,4-dimethyl coumarin

III.



1,2,4-trimethyl coumarin

The trimethyl coumarin no longer possesses the typical coumarin odour. With regard to the coumarin homologue produced by Schmidt from m-homo-salicylic aldehyde according to Perkin's synthesis, the authors arrived at the same conclusion as Chuit and Bölsing, namely that the body obtained by Schmidt represented a mixture

[1]) Berl. Berichte **39** (1906), 871.

[2]) Report April **1096**, 87.

of the isomerides. The methylated coumarines obtained by Fries and Klostermann are attacked in various ways by alcoholates and aqueous alkalies. But as these conditions are obviously very complicated, the two authors continue their experiments, which are intended to show whether laws can be formulated for the formation of coumarinic and isomeric coumarinic acids.

For the quantitative estimation of coumarin in vanilla extracts, see under vanillin, p. 100 of the present Report.

Menthol. With regard to this article we would refer to what we said on p. 58 respecting Japanese peppermint oil.

Musk, Tonquin. The spring season closed with very firm prices, as towards the end of May the stocks were almost completely exhausted, and the forecast is that the prices in the approaching autumn season will not be cheaper.

The shipments of musk during the first half-year of 1906 were as follows: —

Musk export from Shanghai, from 1st January to 30th June 1906.

Year.	Paris	London	New York	Germany and Austria.	Total.
	Catties	Catties	Catties	Catties	Catties
1906	580[1]	—	177	46	**803**[2]
			against:		
1905	278	73	330	40	**721**
1904	489	50	249	50	**838**
1903	616	122	312	134	**1184**
1902	568	125	295	99	**1087**
1901	419	134	254	71	**878**
1900	630	43	174	36	**883**
1899	640	145	186	125	**1096**
1898	859	88	218	86	**1251**

Further reports on this article have unfortunately not come to hand.

Our work on the natural musk aroma which we mentioned already in detail in our last Report[3]), has recently also been published in the technical press[4]).

[1]) A further undetermined quantity sent to Paris per parcel-post is not included in this figure, as such consignments do not pass through the Ch nese custom-house.

[2]) Of which about 85 % Tonquin, and 15 % Sawko, Tampi and Cabardine.

[3]) Report April **1906**, 94.

[4]) H. Walbaum, Das natürliche Moschusaroma. Journ. f. prakt. Chemie II. **73** (1906), 487.

We would once more emphasize the fact that the "artifical musk" met with in commerce is not identical with muskone, but that in this case (as may frequently be observed) there exists only a certain similarity in the odours of two entirely different bodies. For muskone, according to our recent researches, the second of the two formulae $C_{15}H_{28}O$ and $C_{16}H_{30}O$ is the more probable one. By reducing and oxidising muskone, we have already obtained further data on the subject, but we reserve the details of this work for a later communication.

As according to Berthelot's estimates 0,000000000000000001 g. and according to others even smaller quantities of musk are perceptible to the sense of smell, but as on the aggregate condition of evaporated musk different opinions are still held, J. Aitken[1]) has endeavoured to decide experimentally whether a conversion into gas or vapour takes place, or a separation of solid particles. Dust-free moist air was subjected to slight expansions, in which particles possibly present would act as nuclei and cause condensation. As the musk evaporating on condensation of such air had not added to the filtered dust-free air any particle of a larger than molecular size, the conclusion could be drawn that the aggregate condition of evaporating particles of musk is of a gaseous character. According to the same method, the author next examined a large number of other odorous substances; here also, no solid, but only gaseous particles could be found. In further support of the theory that the evaporation of odorous substances depends upon an evolution of gases, Aitken mentions the fact that odorous substances, brought into contact with the mucous membrane of the nose in the form of very fine powders, produce a totally different impression than the act of smelling the same substances. Almost all such very fine powders produce on the mucous membrane direct the same sensation, although their actual odour may differ in a marked degree.

Pollantin. Although the sales of this remedy against hay-fever did not quite come up to our expectations this year, owing to the rainy weather during the flowering season of the gramineæ, we had the satisfaction that this medicament has again during the past season proved efficacious. This applies in a very special degree to the United Kingdom, the classical country of the hay-fever; from patients there we have almost without exception received very good reports of cures, which are partly couched in the most flattering terms, and cannot sufficiently praise the "almost miraculous prompt action of the remedy" — whether in the form of powder or in the liquid state.

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[1]) Proceed. of the Royal Society of Edinburgh **25** (1905), 894. Acc. to Naturwissenschaftliche Rundschau **21** (1906), 98.

In view of the cases of alleged inefficacy of the preparation which occasionally come to our knowledge, we beg to give the following particulars, and propose to return to this subject more in detail in our next Report, i. e. immediately before the commencement of the next hay-fever season.

The inefficacy of pollantin may firstly be due to the fact that the patient is erroneously treated for hay-fever. It is not surprising if in such cases pollantin refuses to act. Secondly, a few patients complain of a certain irritating effect in the application of pollantin. To these we would reply that with every serum, including those which are injected hypodermically (as is well known also with diphtheria serum) many individuals react by local swellings, or slight fever, the so-called "serum-disease". But these symptoms are of course of no consequence whatever for the activity of the serum, and are due to an individual "cannot-tolerate-this", an idiosyncrasy against heterogeneous albumin. In the case of pollantin this manifests itself by itching, or by the flow of tears at the site where it is applied. For determining these idiosyncrasies we supply free on applying a dose of normal serum prepared from horses which have not been treated before, with the same irritating action on serum-sensitive persons as any other animal serum. The above-mentioned symptoms of irritation can be alleviated in such patients, by the administration of smaller doses of the preparation at more frequent intervals. If the result is then also negative, we would ask that details of the case be submitted to us or our Branch Offices direct. We are engaged in working out a special method of application, or a special preparation for such sensitive patients, and hope to communicate our work in this direction in our next Report.

For those who take an interest in the matter, we give below a summary of the literature dealing with hay fever and its treatment:

Bazzicalupo, Gazz. internat. di medicina, March, **1906**.
Dunbar, Zur Ursache und spezif. Heilung des Heufiebers. Munich and Berlin, **1903**.
— Ursache und Behandlung des Heufiebers. Lecture. Leipzig, **1905**.
— Deutsche med. Wochenschr. **1903**, No. 9.
— Berl. klin. Wochenschr. **1903**, No. 24—26, 28.
Kammann, Berl. klin. Wochenschr. **1906**, No. 26.
Liefmann, Zeitschr. f. Hyg. u. Infectionskrankh. **1904**, No. 2,
— Therap. Monatshefte **1905**, No. 12.
— Münch. med. Wochenschr. **1906**, No. 4.
Lübbert, Therap. Monatsh. **1904**, 605.
Lübbert and Prausnitz, Berl. klin. Wochenschr. **1904**, No. 11, 12.
Marcuse, J., Leipziger Illustr. Zeitung, No. 3232, 8th June **1905**.
Prausnitz, Berl. klin. Wochenschr. **1905**, No. 9.
— Münch. med. Wochenschr. **1905**, No. 23.
Wolff-Eisner, Das Heufieber, sein Wesen und seine Behandlung. Munich, **1906**.
— Berl. klin. Wochenschr. **1906**, No. 4.

Safrol. The slight increase in the prices which we have now been compelled to make is of course out of proportion to the rise in the value of the raw material, and for this reason a further advance in the near future may be all the more probable, as our stocks of brown camphor oil, from which safrol is obtained, are becoming seriously depleted. The new supplies which we are still to receive cost much more, and are so unimportant that we have already for some considerable time been unable to enter into any engagements for forward delivery.

Thymol. It has taken a long time before it was possible to raise the selling prices of this preparation, which in consequence of the severe competition and in view of the advance in the price of the raw material, left no longer any profit, for the price-cutting in this article has only recently come to an end. The quotations for "weedseed" (ajowan seed) have advanced during the summer months from 11/- per cwt. to about 14/- per cwt., so that a further increase in our published prices was necessary. With regard to the new harvest in India, of which the first shipments will not reach the market before January/March, the reports from individual districts differ so greatly that it is at present not possible to express an opinion.

Vanillin. The frequent adulteration of vanilla extracts with acetanilide have induced A. L. Winton and E. M. Bailey[1]) to publish the following method for the quantitative estimation of vanillin, coumarin, and acetanilide, which represents a modification of Hess' and Prescott's method. In a suitable vessel 25 g. of the extract are mixed with so much dilute alcohol, that the whole mass amounts to 50 cc., which is then evaporated on the water-bath (not above 70°) down to one half; the manipulation is then repeated once more. Now lead acetate is added until a precipitate is no longer formed; the latter is then filtered and washed out in such a way that the filtrate does not consist of more than 50 cc. This is then shaken first with 20, then 3 times with 15 cc. ether, and the collected ether solutions first with 10, and then 5 times each with 5 cc. of 2 per cent. ammonia liquor. The ethereal portion is then allowed to evaporate at ordinary temperature, the weighed residue is decanted 3 times each with 15 cc. low-boiling petroleum ether (b. p. 30 to 40°), and the petroleum ether poured off is also allowed to evaporate at ordinary temperature. The ethereal extract then contains the coumarin; any acetanilide which has been added is present in the petroleum ether extract.

The coumarin should melt at 67°, the acetanilide has the melting point 112°. If the above-mentioned ammoniacal solution is now acidulated with hydrochloric acid, and extracted with ether, the residue,

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[1]) Pharmaceutical Journal **75** (1905), 476.

after driving off the ether, should melt at 80° (m. p. of vanillin). In order to detect acetanilide, the residue is once more dissolved in 15 cc. of a 10 per cent. ammonia solution, and shaken with the same volume ether. If the ether is driven off, and the weighed residue subtracted from the first, the quantity of pure vanillin is obtained. Any acetanilide found is added to the quantity already ascertained above.

Notes on recent research work concerning terpenes and terpene derivatives.

General.

The researches of L. Balbiano[1]) and his collaborators (already repeatedly described by us) on the action of solutions of mercuric acetate on terpenes and compounds with a propenyl-group, are now supplemented by the authors as follows[2]): The hexylene[3]), C_6H_{12}, of the constitution $(CH_3)_2C:CHCH_2CH_3$, detected in American petroleum, was identified by its oxidation products acetone and propionic aldehyde. — Anethol glycol melts at 98°; the nature of the yellow oil which the authors obtained in addition to this glycol has not yet been determined with certainty. — With regard to the oxidation of methyl chavicol, it may be added that the isomeric chlorine compound $C_{10}H_{13}O_2HgCl$ apparently (?) melts at 91°; of the analogous bromine derivatives the one melts at 70 to 71°, and is crystalline, the other is amorphous. Reduction of the two chlorine derivatives with zinc and soda liquor yielded only methyl chavicol. — The quantities of the isomerides $CH_2O_2:C_6H_3\cdot C_3H_5(OH)\cdot HgC_2H_3O_2$ formed by the action of mercuric acetate on safrol, vary according to the length of time of the action. Both again yield safrol when distilled with phosphoric acid, or when decomposed with sulphuretted hydrogen. The compounds $C_{10}H_{11}O_3N$ (m. p. 89°) and $C_{11}H_{13}O_3N_3$ (m. p. 158°), correspond to the oxime and the semicarbazone respectively of isosafrol glycol. — The compound obtained on oxidation of methyl isoeugenol $(CH_3O)_2:C_6H_3\cdot C_3H_5(OH)_2$, m. p. 120 to 121°, yields in absolute benzene solution with phenyl isocyanate the corresponding carbamic acid ester of the m. p. 166 to 168°,

$$(CH_3O)_2:C_6H_3\cdot CH[OC(:O)\cdot NH\cdot C_6H_5]CH[OC(:O)NH\cdot C_6H_5]CH_3.$$

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[1]) Berl. Berichte **35** (1902), 2994; Report April **1903**, 83 and Berl. Berichte **36** (1903), 3575; Report April **1904**, 100.

[2]) Gazz. chim. ital. **36** (1906), I, 237, 251, 257, 264, 268, 276, 281, 286, 291, 301. Acc. Chem. Centralbl. **1906**, II. 119 to 122; 126.

[3]) Chem.-Ztg. **25** (1901), 932.

The isomeric oxidation-product of methyl isoeugenol (m. p. 87,5 to 88,5°) could be converted after treatment with zinc and soda liquor into a semicarbazone (m. p. 176 to 177°), which proved to be identical with the one produced from the other isomeride. — The constitution of asarone is confirmed by its behaviour towards mercuric acetate; instead of the glycol, there resulted, with loss of water, the aldehyde $C_{12}H_{16}O_4$ (m. p. 47 to 48°, b. p. 184° [15 mm. pressure]; semicarbazone, m. p. 157 to 158°). — By loss of water from the glycols of the propenyl compounds, there are consequently formed the corresponding aldehydes, and of two possible formulæ $R \cdot CH_2 \cdot CH_2 \cdot CHO$ and $R \cdot CH(CH_3) \cdot CHO$, the former belongs to these. The aldehyde $CH_3O \cdot C_6H_4 \cdot CH_2 \cdot CH_2 \cdot CHO$ obtained from anethol glycol, boils at 132 to 135° (10 mm. pressure), its semicarbazone melts at 174°. The aldehyde $CH_2O_2 \cdot C_6H_3 \cdot C_2H_4 \cdot CHO$ produced from isosafrol glycol boils at 140 to 145° (2 mm. pressure). It yields an oxime (m. p. 89°) and a semicarbazone (m. p. 158°). The boiling point of the aldehyde produced from methyl isoeugenol glycol lies at 146 to 147°, the m. p. of its semicarbazone at 176 to 177°, that of the oxime at 62,5 to 63°. — The product resulting from the action of mercuric acetate on l-pinene, Δ_6-6-oxymenthene-2-one, was identified by its oxime (m. p. 138,5°) and its semicarbazone (m. p. 175 to 176°). — The mercury compound from camphene melts at 188 to 189°. The corresponding chlorine compound $C_{10}H_{16}O(HgCl)_2$, becomes pasty towards 150°, but does not yet melt at 230°, and yields again camphene when treated with zinc and soda liquor.

In April 1903 [1]) we had already employed the reaction discovered by Balbiano and Paolini, in order to adopt it if possible for the detection of camphene in essential oils. We regenerated at the time the camphene mercuric acetate by means of sulphuretted hydrogen. Yet the isolation of camphene from Ceylon citronella oil was difficult and incomplete. The melting and boiling points of the distillation-product driven over with water vapour agreed, however, with those of camphene.

Bibliographical notes.

With regard to the continuation of I. W. Brandel's [2]) work: "The Volatile Oils 1904", we may confine ourselves to a simple reference; the essential parts of its contents have already been communicated in our Reports more or less in detail.

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[1]) Comp. Report April **1903**, 84.

[2]) Pharm. Review **24** (1906), 87 and 112; comp. also Report April **1906**, 101.

Analytical notes.

By employing the methods of Thorpe and Holmes[1]), Allen[2]), and the Association of Official Agricultural Chemists of America[3]), E. A. Mann[4]) has determined the alcohol-content of essences, and has found that all three methods give the same results as when the alcohol-content of the distillate is ascertained pycnometrically. In the author's opinion the American method is to be preferred in many cases on account of its simplicity, but clear distillates are not always obtained, and the same remark applies to Allen's method. Thorpe's determination is without doubt the most certain one, but it requires a little more time than the others.

The procedure in the above-named methods is as follows: According to Thorpe and Holmes, 100 vol. water are added to 25 vol. of the sample, the mixture is saturated with salt, and shaken for 5 minutes with 70 vol. petroleum ether (b. p. below 60°). After separating off the aqueous layer, the petroleum ether is vigorously shaken with 25 vol. of a saturated solution of salt. The aqueous portion is now added to the original one, and of the total quantity 100 vol. are carefully distilled over. The alcohol-content of the distillate obtained has to be multiplied with 4. — According to Allen the sample is diluted with water to the 8-fold quantity, calcium chloride and sodium biphosphate added, 100 vol. filtered and distilled. The alcohol-content of the distillate ascertained has to be multiplied with 8. — The method of Association of Official Agricultural Chemists of America requires the addition of the 3-fold quantity of water to the sample in question, and further the addition of magnesium carbonate. After shaking, 100 cc. are filtered off and distilled. The alcohol-content found must then be multiplied with 4.

On the reaction of phenyl hydrazin with the aldehydes and ketones contained in essential oils Benedikt and Strache[5]) have founded a method for determining quantitatively the carbonyl-group of these bodies. The method is based upon the oxidation of the non-combined phenyl hydrazin with Fehling's solution, and measurement of the nitrogen evolved. This method which, as far as we know, has not been introduced in the technical industries, has recently been modified by Watson Smith jun.[6]) in so far, that for driving over the nitrogen no longer steam is used, but a current of carbonic acid

1) Journ. Soc. chem. Industry **22** (1903), 232.
2) Commercial Organic Analysis. 3rd Ed., I, 162.
3) Bulletin 46, U. S. Department of Agriculture, and Food Analysis und Inspection, Leach.
4) Journ. Soc. chem. Industry **24** (1905), 1284.
5) Monatsh. f. Chem. **14** (1893), 273. Acc. to Chem. Centralbl. **1893**, II. 168.
6) Chem. News **93** (1906), 83. Acc. to Chem. Centralbl. **1906**, I. 1289.

The principle of Strache's method remains. For the purpose of absorbing the benzene formed, a mixture of molecular quantities sulphuric acid and nitric acid was found to be very suitable. The method is briefly as follows: In a boiling flask (750 to 1000 cc.) with a stopper provided with 3 holes, are inserted a supply tube for the carbonic acid, a separating funnel, reaching almost to the bottom, with its end bent round, and a Liebig's condenser placed obliquely upwards. To this is joined a bulb-shaped absorption tube bent first straight down, and then slantingly upwards, then, connected by means of a washing bottle, a Schiff's azotometer. After mixing 0,1 to 0,5 g. of the substance in a 100 cc. flask with a measured quantity of 5 per cent. phenyl hydrazin and $1^1/_2$ times the quantity of 10 per cent. sodium acetate, diluting with water to about 50 cc., heating for 15 minutes on a water bath, the flask after cooling is filled up to the mark. The air in the apparatus has been displaced by carbonic acid, and 10 cc. of the phenyl hydrazin solution are now made up with sodium acetate and water to 100 cc.; 50 cc. are admitted through the separating funnel into the boiling flask containing 200 cc. Fehling's solution, by means of which operation the quantity of nitrogen evolved by the phenyl hydrazin is d ter.nined. Next the principal test is made with the substance; each cc. difference of N in both determinations equals 1,252 mg. CO.

Whether this modified Strache's method will be more largely employed than the original one can only be proved by a thorough further test of its practical applicability.

E. Beckmann[1]) has jointly with Danckwortt worked out a new method for testing spices and similar substances, according to which the object under examination is extracted with a suitable solvent and the quantity of the substance dissolved determined on the basis of the increase of the boiling point, or the lowering of the freezing point. For the examination of spices the solvent which has answered best is ethylene bromide. The extracts from 5 g. of the spice in question with 30 g. ethylene bromide, showed the following depressions: anise 0,8°; mace (Banda) 2,46°; cloves (dry) 2,18°; cloves (moist) 2,24°; pepper (white) 0,87°; mustard (black) 0,58°. Moist spices (comp. cloves) show therefore a larger depression; the water-content consequently exerts a certain, though only slight influence. If the method is to be applied to the estimation of the essential oil in aromatic waters, the latter are extracted with ethylene bromide, and the above-named constants are ascertained on the one hand in pure ethylene bromide, on the other in the ethylene bromide used in the extraction. It should be noted that any alcohol present must be removed by shaking the ethylene bromide solution with water, and that the maximum

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[1]) Pharm. Zeitg. **51** (1906), 502, 513.

depression which the water causes in the ethylene bromide must be deducted from the depressions obtained.

Physical notes.

We have before us a work by Th. M. Lowry[1]) on dynamic isomerism in camphor halogen derivatives, and one by him and H. Magson jointly on dynamic isomerism in sulphonic acid derivatives of camphor. The experiments of these two authors form a continuation of those of F. S. Kipping[2]) who succeeded in demonstrating that the sulphonic acids of α-chloro and α-bromo camphor, as well as the simple halogen derivatives themselves, yield isomerides. Now while Kipping's experiments throw light on the chemical side of these processes, in Lowry's and Magson's work the physical side of the bodies to be examined is brought more to the foreground. The substances examined were α- and β-bromo camphor and α-chloro camphor, α-, β-, and α, π-dibromo camphor, α-, β-, and α, π-chloro bromo camphor. The solubilities were determined by evaporating weighed quantities of saturated solutions in weighing-vessels. The specific gravity was determined by means of a self-constructed graduated pipette. The determination of the rotatory power was accomplished in a polarisation apparatus graduated to read down to 0,001°. The proportionate quantities in which the isomerides are in equilibrium in the solution were measured, and finally the rapidity of the isomeric change ascertained. With regard to dynamic occurrences of isomerism in sulphonic derivatives of camphor, there were examined first the derivatives of camphor π-sulphonic acid, and subsequently those of camphor β-sulphonic acid, and of the latter the potassium salts, the amides and anhydramides, the anilides and piperidides. The method of examination is analogous to that of the halogen derivatives of camphor.

Pharmacologico-physiological notes.

From A. J. J. Vandevelde[3]) has appeared a III. communication on the determination of the toxic action of chemical compounds by hæmatolysis. The work comprises the determination of the toxic ratio of various so-called "etherols" *(Äthrole)*[4]), higher alcohols, etc. which were treated similarly to previous objects of examination[5]). We would mention, among others, terpineol, clove oil, peppermint "etherol", eucalyptus "etherol", lavender oil, lemon oil, etc. The experiments showed that the "etherols" are not more poisonous than ordinary essential oils. The toxicity increases with the number of carbon atoms.

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[1]) Journ. chem. Soc. **89** (1906), 1033, 1042.
[2]) Proceed. Chem. Soc. **21** (1905), 124, 125.
[3]) Chem.-Zeitg. **30** (1906), 296.
[4]) Comp. Pharm. Centralh. **46** (1905), 818.
[5]) Comp. Report April **1906**, 103.

Phyto-physiological notes.

In our last Report we have already referred to the work published by E. Charabot and G. Laloue[1]) on the formation and distribution of terpene compounds in the sweet orange tree. We now abstract from the last Report from Roure-Bertrand Fils[2]) two interesting studies on the formation and distribution of the essential oil and on the gradual distribution of the terpene compounds in the various organs of the plant. The experimental plant was in both cases *Artemisia absynthium* L. The first-named experiments showed once more that the essential oil is present in abundance in the plant which is yet quite young. Up to the time of the flowering season the content of odorous substances increases, also with regard to the absolute quantity. But then a decrease in the percentage, as well as in the absolute quantity of oil, takes place. This quantity of oil is used up when after the flowering period the act of fructification is accomplished. Although it is not excluded that during this period a new formation of odorous substances takes place, it is not equal to the quantity consumed. The conclusion drawn by Roure-Bertrand Fils from the results obtained is this, that the essential oils in the plant are recognised as the substances which are used up in the organism in order to ensure the continuance of the species. The results are reproduced graphically in the Report; they show that the root of the young wormwood shrub does not yet contain any oil, the stalk comparatively little, but that the leaf contains the bulk. At the commencement of the flowering period the oil makes its appearance in the root, where its quantity increases steadily, also according to the absolute weight. The loss of essential oil which can be demonstrated during fructification is borne by the leaves, stalks and inflorescences. With regard to the distribution and development of the terpene compounds in the organs of the plant, the examination included the comparative determinations of the essential oil present in the individual organs, as well as the relative solubility of the individual constituents. A long time before the first inflorescences make their appearance, the essential oil of the plant only contains traces of thujone; the oil of the stalks is more difficult soluble than that of the leaves. Immediately after the occurrence of the first inflorescences, the oil contained in these also shows a lower solubility than the oil of the leaves. The ester-content is largest in the roots, and smaller in the stalks, inflorescences and leaves. The content of free thujyl alcohol does not differ largely in the various organs of the plant. Thujone is chiefly present in the leaves, and only traces of it are found in the stalks.

[1]) Compt. rend. **142** (1906), 798; comp. Report April **1906**, 104.
[2]) Berichte, Roure-Bertrand Fils, April **1906**, 1.

From a reprint received by us from Mr. M. Greshoff[1]), we abstract a summary of those plants in which up to the present prussic acid has been detected. It is found in numerous families of the *polypetales* and *gamopetales,* whilst it could only be detected in a few families of *monochlamydæ, monocotyledones,* and *gymnospermæ.* In the *cryptogamæ* only one family comes up to the present under consideration, and of that only one case in which the detection of prussic acid can be accepted as beyond doubt.

Hydrocarbons.

F. W. Kay and W. H. Perkin jun.[2]) continue their experiments on the synthesis of terpenes (part VIII), with the synthesis of the optically active modifications of Δ_8-p-menthenol-8 and $\Delta_{3,8(9)}$-menthadiene. The crude product for the former was the ethyl ester of Δ_1-tetrahydro-p-toluic acid, which, when treated with the theoretical quantity of magnesium methyl iodide, and then decomposed with water and dilute acid, is converted into l-Δ_8-p-menthenol-8,

$$CH_3 \cdot CH \left\langle \begin{array}{l} CH_2 - CH \\ CH_2 \cdot CH_2 \end{array} \right\rangle C \cdot C(CH_3)_2 \cdot OH$$

b. p. 100° at 14 mm. pressure; $\alpha_D - 67°$. If the latter is treated with potassium bisulphate, a partial racemism takes place and there is formed l-$\Delta_{3,8(9)}$-p-menthadiene,

$$CH_3 \cdot CH \left\langle \begin{array}{l} CH_2 - CH \\ CH_2 - CH_2 \end{array} \right\rangle C \cdot C \left\langle \begin{array}{l} CH_2 \\ CH_3 \end{array} \right.$$

with a dipentene-like odour, b. p. 185° at 748 mm. pressure; $[\alpha]_D - 10{,}0°$ (benzene solution). Pure d-$\Delta_{3,8(9)}$-p-menthadiene was produced by the direct action of magnesium methyl iodide in excess on the d-ester without potassium bisulphate; it boils at 184 to 186° at 756 mm. pressure, and possesses a limonene-like odour; $[\alpha]_D + 98{,}2°$ (benzene solution).

Pinene. In his researches on the pinene series, Wallach[3]) has on the one hand produced the ketone corresponding to nitrosopinene, and on the other hand cleared up the constitution of pinocarvone[4]). By reducing nitrosopinene there is formed pinylamine, $C_{10}H_{15}NH_2$, and, by treating the latter with nitrous acid, pinocarveol, $C_{10}H_{15}OH$, (b. p. 100 to 102° [12 mm. pressure]; d 0,980; $n_{D18°}$ 1,4988). On

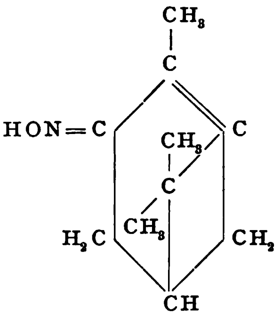
[1]) British Association, York, **1906**. Distribution of Prussic Acid in the Vegetable Kingdom.

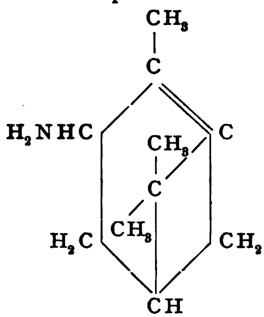
[2]) Journ. chem. Soc. **88** (1906), 839; Proceed. chem. Soc. **22** (1906), 72; comp. Reports October **1904**, 97, October **1905**, 90, 92, April **1906**, 119.

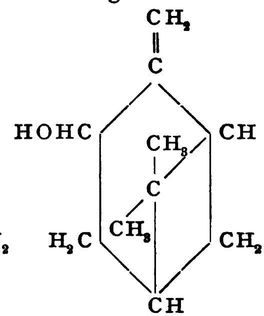
[3]) Liebig's Annalen **346** (1906), 220.

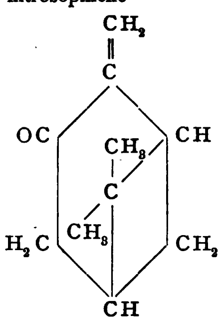
[4]) Liebigs Annalen **277** (1893), 149; **279** (1894), 387; **300** (1898), 28 comp. also Report October **1898**, 47.

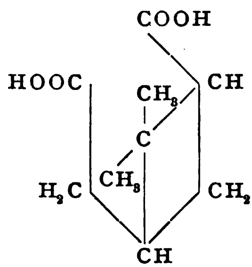
oxidation this yields (though only in small quantity) the corresponding ketone pinocarvone, $C_{10}H_{14}O$. The conversion from pinylamine into pinocarveol is accomplished without ring-disruption, and the fact that the grouping of the carbon atoms in both compounds is still the same, is proved by the ready formation of cymene, for example when boiling with aqueous sulphuric acid (1 in 2). For pinocarvone Wallach accepts the enolic form $C_{10}H_{13}OH$ of a ketone with one ethylene-linking. The ketone regenerated from the semicarbazone (m. p. 204°) boils at 95° (12 mm. pressure); d 0,984; n_{D20° 1,5050; the results agree with those previously obtained[1]). The reduction of pinocarvoxime (melting at 98°) in alcoholic solution with sodium resulted in a base, b. p. 87 to 88° (12 mm. pressure), which differed totally from pinylamine. The acid $C_9H_{14}O_4$, b. p. 170 to 180° (12 mm. pressure), formed by oxidation of pinocarvone with permanganate (1 %), melts at 96 to 97°, and is dibasic. Apart from its somewhat low melting point, it resembles pinic acid in a remarkable manner. The conversion into this acid is accomplished in the following manner: —


nitrosopinene


pinylamine


pinocarveol


pinocarvone

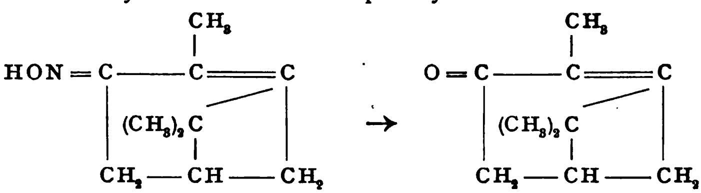

pinic acid

When pinylamine is treated with nitrous acid, a displacement of the ethylene-linking takes place, which explains the constitution of

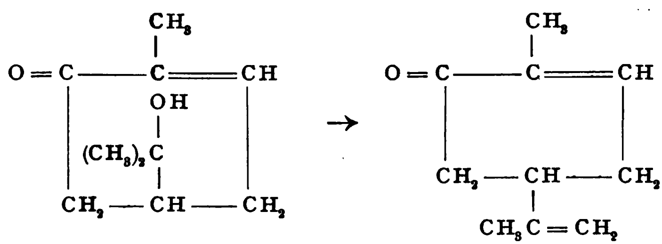
1) loc. cit.

the last formulæ. The question, why also in pinocarvone the picean-ring does not readily open, and no conversion of pinocarvone into carvone takes place, is one that remains for the present unsolved [1]). — On the alcohol discovered by us in the oil of *Eucalyptus Globulus* Lab., whose properties, according to Wallach, corresponded with those of pinocarveol, we have already reported [2]).

When boiled with hydrochloric acid, nitrosopinene, according to Kremers and v. Baeyer, yields carvacrol. By distillation of nitrosopinene with oxalic acid repeated more than 25 times, Wallach has obtained in a small yield (3 to 4%) an intermediate product of this decomposition, carvopinone, the ketone corresponding to nitrosopinene, of the b. p. 94 to 96° (12 mm. pressure). But even when oxalic acid is used, the ketone separated off undergoes a partial isomerisation into carvone; mineral acids accelerate this process. The prisms of the semicarbazone do not yet melt above 300°, and are decomposed only at a still higher temperature. Carvopinone, whose production in the pure state is extremely difficult, cannot be regenerated in an absolutely unchanged form from the semicarbazone, at it is partly isomerised into carvone. By reducing crude carvopinone with sodium, and oxidising the reduction-product obtained with chromic acid, pinocamphone, $C_{10}H_{16}O$, was obtained, whose semicarbazone melts at 208°. Now the direct conversion of the nitrosopinene into carvone, with oxalic acid or hydrochloric acid, also succeeded; in the latter case it always contains a small quantity of carvacrol.



nitrosopinene → carvopinone



(intermediate product) → carvone

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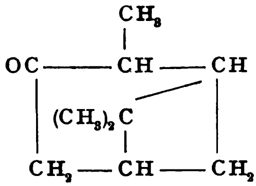
[1]) Comp. however also similar conditions under pinocamphone and pinic acid.

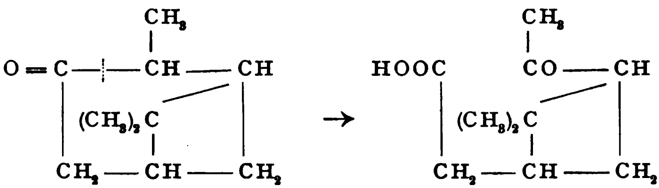
[2]) Report October **1905**, 33; comp. Gildemeister and Hoffmann, The Volatile Oils, p. 528.

Pinocamphone, to which, on the strength of what has been said above, the formula



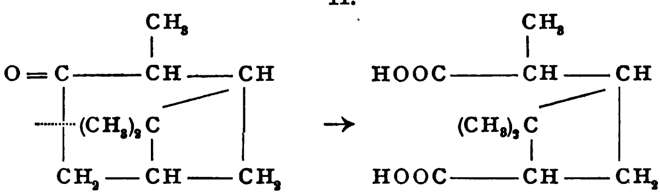
belongs, was identified by its dibromide (m. p. 118 to 119°), and by oxidation with chromic acid mixture or permanganate. In both cases there is formed, besides a keto acid, a dibasic acid, both of which have the same carbon-content as the crude material. The keto acid $C_{10}H_{16}O_3$ (α-pinonic acid), regenerated from its semicarbazone (m. p. 203°), melted at 103 to 104°. The dibasic acid $C_{10}H_{16}O_4$ (m. p. 186 to 187°), isomeric with camphoric acid, was identified among others by its silver salt. The process pinocamphone → α-pinonic acid (or the dicarboxylic acid) is explained by the following graphic formulæ:

I.



pinocamphone → pinonic acid

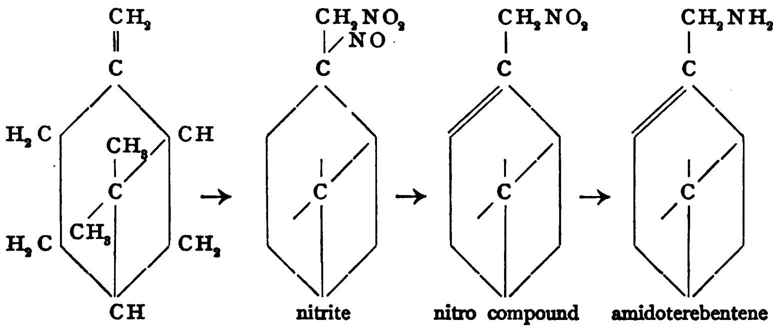
II.



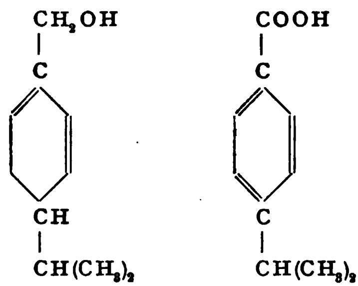
pinocamphone → dicarboxylic acid

The production of pinylamine has been greatly simplified by Wallach in this manner, that he evaporates to dryness the lyes formed in the reduction of nitrosopinene with zinc and acetic acid, supersaturates them with lime in a copper still, and rectifies *in vacuo* the pinylamine distilled with vapour. Further control-experiments proved that as a matter of fact pinylamine is the base belonging to carvopinone, for on oxidation with 1 per cent. potassium permanganate solution it passes over directly into that ketone.

A control of the nitroterebentene, $C_{10}H_{15}NO_2$, previously obtained by Pesci and Bettelli[1]) by the action of nitrous acid on pinene and subsequent treatment with ammonia, and of its reduction-product amidoterebentene, $C_{10}H_{15}NH_2$, (b. p. 95° [12 mm. pressure]; d 0,9325; $n_{D19°}$ 1,4960), led to the conclusion that in amidoterebentene the amido-group is situated in the side-chain, analogous to the conditions ascertained in β-phellandrene[2]). Further, it may be assumed that the base is derived from a methene terpene and that nopinene must be regarded as the fundamental hydrocarbon. The alcohol obtained from amidoterebentene oxalate by conversion with sodium nitrite yields on oxidation with chromic acid first of all a substance with an odour like cuminic aldehyde, whose semicarbazone melts at 201 to 203°, and then an acid (m. p. 115°) which beyond doubt represents cuminic acid. For this reason amidoterebentene should contain the picean-ring with only one ethylene-linking, the ring splitting up into the hydrocumin (or cumin) ring: —



nopinene — nitrite — nitro compound — amidoterebentene



alcohol — cuminic acid

In continuation of his experiments to convert two isomeric terpene haloid hydrates to some extent quantitatively into a magnesium com-

[1]) Gazz. chim. ital. **16** (1886), 337.
[2]) Liebig's Analen **340** (1905), 1; Report October **1905**, 97.

pound by means of Grignard's reaction, A. Hesse[1]) gives some interesting information on the relations between pinene hydrochloride and camphene hydrochloride. Both can be converted by means of a new method, with a yield of 70 to 80 %, into a magnesium compound. When decomposed with water both magnesium compounds supply the same camphane of the m. p. 153° in a very good yield. It is therefore proved that the two terpene hydrochlorides possess the same carbon skeleton. Pinene hydrochloride magnesium, when exposed to the air, briskly absorbs oxygen, and the decomposition of the oxidised magnesium compound by water takes place less briskly than that of the non-oxidised compound, when at the same time abundant quantities of borneol are formed. The experiments also served for elucidating the relationship between borneol and isoborneol and the relation in which the two alcohols stand to the above-mentioned hydrochlorides. According to the well-known patents, isoborneol in benzene solution is converted into camphor by oxidation with aqueous dilute permaganate, with ozone, with hot air, or by the introduction of chlorine or nitrous vapours. In the case of isoborneol, the reaction is in many oxidation-methods accomplished more readily than in the case of borneol. But as all endeavours to detect an isomeric camphor in the oxidation-products were unsuccessful, Hesse believes that borneol and isoborneol are stereo-isomeric, in support of which may be mentioned the conversion of isoborneol in xylene solution, by sodium, into borneol, and for which Hesse himself supplies fresh proofs. His method for the production of organo-magnesium compounds is chiefly based upon this, that the solution of hydrochlorides is added to the magnesium whilst a primarily initiated reaction of the magnesium with briskly reacting alkyl halogenides is still proceeding. By this method Hesse converts 80 to 85 % of the pinene hydrochloride into the magnesium compound $C_{10}H_{17}MgCl$, whilst 10 to 15 % react in the well-known manner according to the equation: —

$$2\,C_{10}H_{17}Cl + Mg = MgCl_2 + (C_{10}H_{17})_2$$

and the remainder of the reaction-product is formed of small quantities of camphene and camphane. The final product of the reaction is generally free from chlorine. Hesse concludes from his experiments that in this Grignard's reaction not the alkyl halogenides, but the alkylmagnesium halogenides formed during the primary reaction, initiate the reaction. This process was also accomplished without difficulties with camphene hydrochloride; about 60 % reacted with the magnesium, with formation of $C_{10}H_{17}MgCl$; 20 % formed $(C_{10}H_{17})_2$; and the general properties of this hydrocarbon point to its identity with the one obtained from pinene hydrochloride.

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[1]) Berl. Berichte **39** (1906), 1127.

But both are hardly attacked by oxidising agents; for this reason the unobjectionable proof of their identity is difficult, and isomerism is not entirely excluded. Hesse summarises his experiments in the following sentences: Pinene hydrochloride is bornyl chloride, and has the same carbon skeleton as camphene hydrochloride. The chlorine atom of the principal portion of the camphene hydrochloride must be attached to the same carbon atom as that to which the chlorine atom in pinene hydrochloride is attacked. Both hydrochlorides have consequently an identical structure, and their differences can only be explained by stereo-isomerism. Borneol which was abundantly obtained from both hydrochlorides, and isoborneol obtained in larger quantities only from camphene hydrochloride, are stereo-isomeric secondary alcohols. On the much-debated question of the constitution of camphene, Hesse's researches do not give a direct answer. The experimental part of the work contains in the first place the discussion of the various reaction-products; next a detailed description of the production of the pinene and camphene magnesium chlorides respectively, the action of water on these, and the formation of inactive camphene from both; and finally the oxidation-experiments with the two magnesium compounds.

In order to safeguard his priority respecting the synthesis of borneol from pinene hydrochloride against Hesse, J. Houben[1]) reports on the production of borneol and bornyl acetate from pinene hydrochloride. He obtains by his process up to 72 % of the theoretical yield of borneol. Bornyl acetate he obtains by means of his method[2]) for the esterification of alcohols and phenols.

Some new derivatives of pinene have been produced by F. P. Leach[3]) from pinene nitrosochloride. By treating the latter with alcoholic potassium cyanate at 50 to 60°, a compound $C_{12}H_{17}O_3N_3$ (m. p. 238 to 240°) can be isolated, which dissolves without decomposition in hot concentrated nitric acid, and which by reduction with zinc and acetic acid, with loss of CO_2 and NH_3, forms the compound $C_{11}H_{18}ON_2$ (m. p. 224°) which is also very stable. If the compound $C_{12}H_{17}O_3N_3$ is treated with hot concentrated sulphuric acid, there is formed, with loss of CO_2 and NH_3, a base $C_{10}H_{18}ON_2$ (m. p. 123 to 125°) crystallising in needles. The body is amphoteric, and appears to represent an amine oxime. This can also be obtained by simply allowing NH_3 to act on pinene nitrosochloride.

Limonene. We have already described the action of potassium cyanide on limonene nitrosochlorides according to Tilden and Leach[4]).

1) Berl. Berichte **39** (1906), 1700.
2) Berl. Berichte **39** (1906), 1736; comp. also the present Report, p. 120.
3) Proceed. Chem. Soc. **22** (1906), 137.
4) Journ. Chem. Soc. **85** (1904), 931; Report October **1904**, 112.

It appears that the treatment of α-limonene nitrosochloride with magnesium methyl iodide has given analogous results, as a further work by Tilden conjointly with Sheppeard[1]) shows. The body from β-nitrosochloride recrystallised from alcohol melts at 150°, and is very stable. α-Limonene nitrosochloride, when acted upon by magnesium methyl iodide, yields a body of entirely similar properties; but its melting point (42°) lies considerably lower, and it dissolves also more readily in petroleum ether. The analysis showed that both bodies are formed from the corresponding bimolecular nitrosochlorides by loss of an oxygen atom. By the action of molecular quantities phosphorus pentachloride on the α-compound (24 hours at ordinary temperature) a product $C_{20}H_{32}N_2Cl_4$ of the m. p. 139° is formed; the corresponding product resulting from the action on the β-compound melts at 113°. The constitution of the new bodies has not yet been definitely determined.

Menthene. In a preliminary communication Wallach[2]) publishes experiments, according to which by condensation of 1,4-methylcyclohexanone with bromo isobutyric ester and zinc, conversion of the oxyester formed (b. p. 148 to 150° at 16 mm. pressure) by loss of water into 1,4-methylcyclohexene isobutyric ester (b. p. 123 to 126° at 13 mm. pressure), and by saponification of the latter, an acid $C_{11}H_{18}O_2$ melting at 95 to 96° is formed, which on slow distillation with loss of carbon dioxide yields menthene, $C_{10}H_{18}$. This hydrocarbon was not, however, the ordinary i-Δ_3-menthene, but the yet unknown i-$\Delta_{4(8)}$-menthene,

$$CH_3 \cdot CH \begin{array}{c} \diagup CH_2 \cdot CH_2 \diagdown \\ \\ \diagdown CH_2 \cdot CH_2 \diagup \end{array} C : C(CH_3)_2$$

designated by Wallach also as bihydroterpinolene; b. p. chiefly 172 to 174°; d 0,831; n_{D21° 1,4647. By the action of amyl nitrite and hydrochloric acid, an oil with a deep blue colour is formed gradually solidifying into white crystals. The oil as well as the crystals readily volatilise with water vapour. The crystallised addition-product has a melting point of 101 to 103°. Boiling with dilute sulphuric acid converts the $\Delta_{4(8)}$-menthene into ordinary Δ_3-menthene.

F. W. Semmler[3]) conjointly with Ch. Rimpel, has succeeded in synthesising the $\Delta_{8(9)}$-menthene and the active $\Delta_{3,8(9)}$-menthadiene. The crude material was isopulegol obtained from d-citronellal by Tiemann and Schmidt's method. The former was converted

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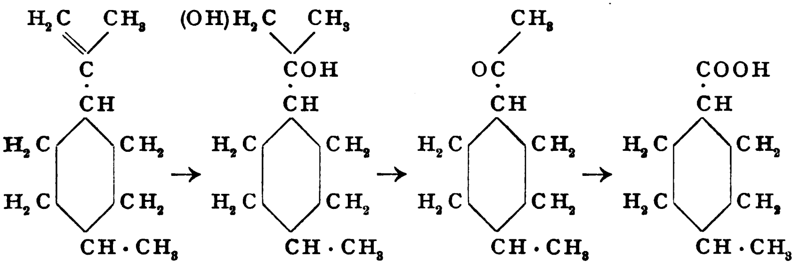
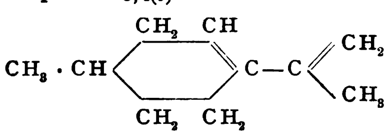
[1]) Journ. Chem. Soc. **89** (1906), 920.
[2]) Berl. Berichte **39** (1906), 2504.
[3]) Berl. Berichte **39** (1906), 2582.

into the chloride (d_{20° 0,9600; α_D 19,15°; n_D 1,47740), this reduced with sodium and absolute alcohol, and the hydrocarbon formed identified as $\Delta_{8(9)}$-menthene, $C_{10}H_{18}$; d_{20° 0,8104; n_D 1,45662; $\alpha_D \pm 0^\circ$. By oxidation with dilute permanganate solution it was possible to isolate p-menthene-8, 9-diol, $C_{10}H_{18}(OH)_2$ (b. p. 165° [26 mm. pressure]); on further oxidation of this glycol with chromic acid there resulted an as yet unknown methyl ketone, $C_9H_{16}O$ (b. p. 70 to 73° [13 mm. pressure]; d_{20° 0,8982; n_D 1,44561; $\alpha_D \pm 0^\circ$), which yielded a semicarbazone (m. p. 164 to 165°) and could be converted with alkaline bromine solution into p-hexahydrotoluic acid, $C_8H_{14}O_2$, m. p. 108°. The progress of the reaction may be explained by the following graphic formulæ: —



Δ 8 (9)-menthene — glycol — ketone $C_9H_{16}O$ — p-hexahydro-toluic acid

When the isopulegol chloride was dissolved in an equal quantity quinoline, and added drop by drop to quinoline heated to 200 to 210°, there was obtained a hydrocarbon $C_{10}H_{16}$ boiling between 62 and 65° (14 mm. pressure), or from 174 to 177° (norm. pressure); d_{20° 0,8420; n_D 1,48422; $\alpha_D + 15^\circ$. From the molecular refraction Semmler and Rimpel infer that it is a terpene with two double-linkings, the one in $\Delta_{8(9)}$- the other in Δ_3- position. It is therefore a question of the terpene $\Delta_{3,8(9)}$- menthadiene:



Methene hydrocarbons. In connection with the methene-suberene[1]) (methene-cycloheptane) described by him, Wallach[2]) gives details of the production of methene-cyclopentane, methene-cyclohexane,

[1]) Liebig's Annalen **345** (1906), 139.
[2]) Liebig's Annalen **347** (1906), 316.

and the three position-isomeric methene-methylcyclohexanes, with reference to the special properties of the methene-group. The crude materials employed were the substituted acetic acids $\genfrac{}{}{0pt}{}{R}{R}\!>\!C(OH) \cdot CH_2 \cdot COOH$, whose esters, as is well known, can be readily obtained by condensation of the cyclic ketones with bromo acetic ester and zinc. It was once more proved that the use of benzene as a diluent increases the yield very advantageously. Of the most simple conversion-products of the methene hydrocarbons, which can be obtained from the acetic acids by splitting off H_2O and CO_2, Wallach mentions in the first place the glycols and nitrosochlorides. The former, $\genfrac{}{}{0pt}{}{R}{R}\!>\!C(OH)CH_2OH$, are formed by oxidation with 1 per cent. permanganate solution, when the hydroxy acids $\genfrac{}{}{0pt}{}{R}{R}\!>\!C(OH)COOH$ and ketones $\genfrac{}{}{0pt}{}{R}{R}\!>\!CO$ are also always obtained as products of further oxidation. The glycols, when treated with acids, yield with elimination of water saturated cyclic aldehydes, $\genfrac{}{}{0pt}{}{R}{R}\!>\!CH \cdot CHO$, alongside of which unsaturated alcohols, $\genfrac{}{}{0pt}{}{R}{R}\!\gg\!C \cdot CH_2OH$, occur in consequence of another progress of reaction. But the properties of the aldehydes themselves which appear so to say as substituted acetic aldehydes, and polymerise readily, have a considerable influence on the yield. The odour of the saturated cyclic aldehydes ranges between that of benzaldehyde and a higher fatty aldehyde. The semicarbazones dissolve comparatively easily in water, but can be purified by recrystallisation from boiling water. The nitrosochlorides of the menthene hydrocarbons can be readily converted with alcoholic solutions of piperidine into the generally well-crystallising nitrolamines $\genfrac{}{}{0pt}{}{R}{R}\!>\!C(NC_5H_{10})CH{=}NOH$, and when hydrochloric acid is abstracted pass over into oximes. These can be split up by hydrolysis into unsaturated aldehydes $\genfrac{}{}{0pt}{}{R}{R}\!\gg\!C \cdot CHO$, which have a much more pronounced benzaldehyde odour, and whose semicarbazones are much more difficultly soluble in water and melt considerably higher than those of the corresponding saturated aldehydes. Of the twelve aldehydes separated off in the form of the semicarbazones, hexahydrobenzaldehyde is the only one which up to the present has been examined more in detail.

Pentacyclic compounds: methene-cyclopentane, $\left.\begin{array}{l}CH_2\,CH_2\\ |\\ CH_2\,CH_2\end{array}\right\rangle C{=}CH_2$, b. p. 78 to 81°; d 0,78; n_{D19° 1,4355. The glycol, $\left.\begin{array}{l}CH_2\,CH_2\\ |\\ CH_2\,CH_2\end{array}\right\rangle C(OH)CH_2OH$, melts at 39 to 41°, and owing to its exceptional solubility cannot be obtained in crystalline form. The semicarbazone of the pentanone isolated from the non-oxidised portions melted at 205 to 207°. Cyclopentane aldehyde, $\left.\begin{array}{l}CH_2\,CH_2\\ |\\ CH_2\,CH_2\end{array}\right\rangle CH\cdot CHO$, split off from the glycol with sulphuric acid (1 in 10), yielded a semicarbazone of the m. p. 123 to 124°. — The nitrolpiperidide of menthene-cyclopentane produced from the nitrosochloride, melted at 116 to 117°. From the nitrosochloride treated with sodium methylate, there is obtained the unsaturated oxime C_6H_8NOH, from which sulphuric acid splits off cyclopentene aldehyde, $\left.\begin{array}{l}CH_2\cdot CH_2\\ |\\ CH_2\cdot CH\end{array}\right\rangle\!\!\!/\!/ C\cdot CHO$, whose semicarbazone melts at 208°. The aldehyde regenerated from it was oxidised by silver oxide into cyclopentene carboxylic acid, C_5H_7COOH, m. p. 119°.

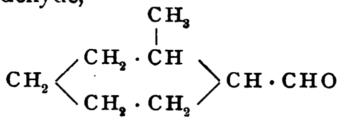
Hexacyclic compounds: methene-cyclohexane,

$$CH_2\left\langle\begin{array}{l}CH_2-CH_2\\ CH_2-CH_2\end{array}\right\rangle C=CH_2$$

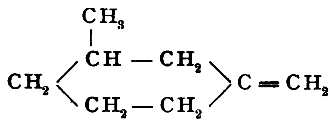
(b. p. 105 to 106°; d 0,8025; n_{D20° 1,4501), has in its properties an extraordinary resemblance to tetrahydrotoluene. The glycol, alongside of which cyclohexanone is formed, crystallises very well, melts at 76 to 77°, and yields, with an equal volume dilute sulphuric acid, by means of steam-distillation, hexahydrobenzaldehyde, $CH_2\left\langle\begin{array}{l}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{array}\right\rangle CH\cdot CHO$, after rectification passing over at ordinary pressure from 161 to 163°; d 0,9263; n_{D19° 1,4495; semicarbazone, m. p. 167 to 168°. The aldehyde has a great capacity for condensation. — The nitrosochloride of methene-cyclohexane yields a nitrolpiperidide of the m. p. 127°, and an oxime giving on distillation with dilute sulphuric acid cyclohexene aldehyde, $CH_2\left\langle\begin{array}{l}CH_2\,CH_2\\ CH_2\,CH\end{array}\right\rangle\!\!\!/\!/ C\cdot CHO$, whose semicarbazone melts at 212 to 213°. — 1,2-methene-methylcyclohexane,

$$\begin{array}{c}\quad CH_3\\ \quad |\end{array}$$
$$CH_2\left\langle\begin{array}{l}CH_2\cdot CH\\ CH_2\cdot CH_2\end{array}\right\rangle C=CH_2$$

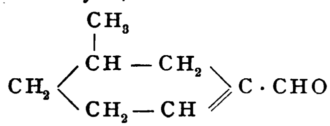
b. p. 122 to 125°; d 0,808; n_{D22° 1,4516. The glycol (in addition to which 1,2-methylhexanone is formed) melts at 59 to 60°. The hexahydro-o-tolyl aldehyde,



obtained from it in small quantities, yields a semicarbazone of the m. p. 136 to 137°. The nitrosochloride of this methene-methylcyclohexane is solid, the nitrolamine syrupy; the oxime yields Δ_1-tetrahydro-o-tolyl aldehyde with an odour of bitter almonds; semicarbazone m. p. 208 to 212°. — 1,3-methene-methylcyclohexane,



b. p. 123 to 124°; d 0,794, or 0,797; n_{D20° 1,4461, n_{D18° 1,4466; $[\alpha]_D$ — 29°. The glycol, b. p. 150 to 153° (39 mm. pressure), yields an aldehyde whit a semicarbazone of the m. p. 158 to 160°. The nitrosochloride of the hydrocarbon yields a nitrolpiperidide of the m. p. 136 to 137°, and with alcoholic potash (application of heat) the oxime of Δ_1-tetrahydro-m-tolyl aldehyde,



whose semicarbazone melts at 206 to 207°. — 1,4-methene-methylcyclohexane, $CH(CH_3)\left\langle\begin{matrix}CH_2 \cdot CH_2\\ CH_2 \cdot CH_2\end{matrix}\right\rangle C = CH_2$, b. p. 122 to 123°; d 0,7925; n_{D22° 1,4446. The glycol, m. p. 86 to 87°, yields only very small quantities of an aldehyde whose semicarbazone melts at 154 to 156°. The nitrosochloride of the hydrocarbon, although formed in small quantity, readily gives a nitrolpiperidide of the m. p. 134 to 135°. The oxime and the Δ_1-tetrahydro-p-tolyl aldehyde from the nitrosochloride are formed easily, and the semicarbazone of the aldehyde melts at 192 to 194°.

Alcohols.

In a lengthy treatise I. Kondakow[1]) criticises on the one hand Bredt's[2]) view on the constitution of borneol and isoborneol, and on

[1]) Chem.-Ztg. **30** (1906), 497.

[2]) Studie über die räumliche Konfiguration des Kampfers und einiger seiner wichtigsten Derivate; Leipzig 1905, Veit & Co.; Report October **1905**, 86.

the other hand the opinion held by Semmler[1]) on the structure of isomeric fenchyl alcohols and fenchone. After introductory historical observations on the constitution of bornyl alcohols, the author attacks Bredt's view according to which borneol and isoborneol must be looked upon as secondary alcohols, stereo isomeric with each other. But — Kondakow thinks — so long as the conditions prevailing in the conversion of borneol, and especially of isoborneol, into bornylene or camphene respectively, have not been elucidated with unobjectionable uniform material, and the identity of the two isoborneols originating from camphene and from camphor has not been proved, no further conclusions on the constitution of these alcohols should be drawn. On the strength of the present experimental material, Kondakow wishes in the first place to emphasize the tertiary character of isoborneol.

With regard to the remarks made by the author on an isoborneol preparation originating from our factory, which Biltz had examined for its cryoscopic behaviour, we wish, however, to reply that it would only have been necessary for Mr. Kondakow to address himself personally to us, if the question of the production of our isoborneol had interested him for his studies. We would then, of course, have been glad to inform him that the preparation in question had been produced by the universally known method, by means of glacial acetic acid and sulphuric acid from the camphene of citronella oil.

Kondakow further expresses himself in disagreement with Semmler's[2]) new fenchone formula. The oxidation-result (formation of isocamphoronic acid and dimethyltricarballylic acid) is, if a re-arrangement is accepted, explained equally well in Wallach's fenchone formula. Semmler's view on the formation of m-cymene from fenchone seems to Kondakow somewhat far-fetched, and one-sided. The conclusions which Semmler, by comparing the physical properties of camphor and fenchocamphorone on the one hand, and fenchone and camphenilone on the other, draws on the constitution of these bodies, appear to Kondakow somewhat risky, in view of the present inadequate observation-material. With regard to the detailed discussion on the constitution of the haloid anhydrides and fenchenes from the two fenchyl alcohols, into which Kondakow enters at the end of his work, and which is chiefly of a purely hypothetical character, we need here not go further into.

It is a well known fact that the esterification of sensitive and especially of tertiary alcohols is accompanied by great difficulties.

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[1]) Chem.-Ztg. **29** (1905), 1313; Report April **1906**, 124.
[2]) loc. cit.

J. Houben[1]) now has endeavoured to make use for this purpose of Grignard's magnesium compounds, which, as is well known, react with alcohols, with formation of halogen magnesium alcoholates: —

$$ROH + R_1MgI = R\cdot OMgI + R_1H.$$

These are now converted with acetic anhydride or other anhydrides (or their chlorides) into the esters, according to the following equation:

$$R\cdot OMgHlg + (CH_3\cdot CO)_2O = R\cdot O\cdot COCH_3 + CH_3COOMgHlg.$$

In esterifying tertiary alcohols, only the chlorine magnesium compounds could be used successfully; ethyl-, methyl-, or benzylmagnesium chloride gave about the same results, viz., a yield of 93 to 98 % ester. Products absolutely free from chlorine could only be obtained with methyl magnesium chloride. In this manner there were produced acetic esters of geraniol, linalool, terpineol, isoamyl alcohol, thymol and terpin, and further also the propionic esters of linalool and terpineol.

The author's opinion that terpinyl acetate can only be produced by his method, is, however, not correct, as we have obtained this ester also very conveniently and in abundant quantity by boiling with acetic anhydride.

Borneol. From their researches on benzyl and phenyl borneols, and their dehydration-products, A. Haller and E. Bauer[2]) come to the conclusion that there are formed on the one hand α-benzyl camphenes (provided that the designation α for the substitution in the CH_2-group of camphor is retained) and on the other β-benzyl and phenyl camphenes, if the position at the carbon atom of the radical CO is designated with β. From secondary α-benzyl borneol

$$C_8H_{14}\left\langle\begin{array}{l}CH\cdot CH_2\cdot C_6H_5\\ |\\ CH\cdot OH\end{array}\right.$$

the production of α-benzyl camphene can be accomplished in various ways, but the angles of rotation of the individual products are different. By abstracting water by means of phthalic anhydride, a hydrocarbon of $[\alpha]_D + 8°20'$ is obtained; by formic acid one of $[\alpha]_D + 5°20'$ and by pyruvic acid one of $[\alpha]_D + 1°25'$. From tertiary β-benzyl borneol

$$C_8H_{14}\left\langle\begin{array}{l}CH_2\\ |\\ C\left\langle\begin{array}{l}CH_2C_6H_5\\ OH\end{array}\right.\end{array}\right.$$

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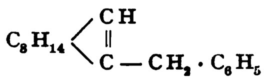
[1]) Berl. Berichte **39** (1906), 1736. Comp. also German Patent No. 162863, Chem. Centralbl. **1905**, II. 1060.

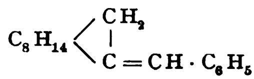
[2]) Compt. rend. **142** (1906), 677.

β-benzyl camphene can readily be obtained by dehydration with the application of heat, by means of the above-mentioned reagents. This isomeride of α-benzyl camphene passes over at 150 to 161° (11 mm. pressure), crystallises in a freezing mixture into needles melting at 24°, and has in alcoholic solution the rotatory power $[\alpha]_D - 60° 44'$. But this is not the only hydrocarbon formed. Haller and Bauer have, besides the crystals, also separated off an oil which appears to be a liquid isomeride of the solid body. For the two the following formulæ would apply: —

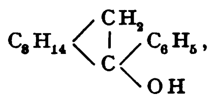
I.



II.

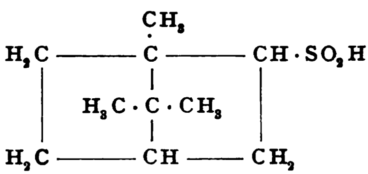


From tertiary phenyl borneol



β-phenyl camphene is formed quantitatively by heating with pyruvic acid. It represents an oil passing over at 138 to 141° (10 mm. pressure); $d_{11°}^{18°}$ 0,9736; $[\alpha]_D + 7° 15'$.

It is well known that J. Houben and L. Kesselkaul[1]), and recently also A. Hesse[2]) have studied the conversion of pinene hydrochloride into the corresponding organomagnesium compound. The former then obtained, by the action of carbon dioxide on the reaction-mixture, hydropinene carboxylic acid. W. Borsche and W. Lange[3]) have now obtained by means of sulphur dioxide from the magnesium compound of pinene hydrochloride, camphane-2-sulphinic acid



This acid, also designated by the authors "camphyl sulphinic acid", can readily be converted into its bromide, from which by reduction with tin and hydrochloric acid camphyl sulphydrate (thioborneol)

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[1]) Berl. Berichte **35** (1902), 2519 and 3695; **38** (1905), 3796; Report April **1906**, 116.

[2]) Berl. Berichte **39** (1906), 1127; comp. also the present Report, p. 111.

[3]) Berl. Berichte **39** (1906), 2346.

$C_{10}H_{17}\cdot SH$ is formed. This was also obtained by the direct action of sulphur on camphyl magnesium chloride. Both products boiled at normal pressure between 205 and 215°, and were identified as thioborneol, which at ordinary temperature possesses only a faint odour at the same time like camphor and mercaptane, is almost insoluble in water, but is absorbed by alkali liquor as well as by organic solvents. When exposed to the air it oxidises to camphyldisulphide $(C_{10}H_{17})_2S_2$ of the m.p. 121° which is insoluble in alkalies. By the action of mercuric chloride on thioborneol in alcoholic solution, thiobornyl mercuric chloride was obtained which decomposes above 300° without melting.

Terpineol. O. Wallach[1]) has continued his work on the terpineol of the m.p. 32°[2]) designated by him as β-terpineol, and has produced by addition of NOCl, N_2O_4, and N_2O_3, the previously described β-terpineol nitrosochloride (m.p. 103°), and also the nitrosate (m.p. 125°), and the nitrosite (m.p. about 78°), although the last-named only in a small yield. For the further reactions the nitrosochloride was employed. It appears that by the action of sodium methylate an hydroxy-oxime is formed from it, for on boiling with acids, hydroxylamine and water are split off, and a body of the composition $C_{10}H_{14}O$ is formed. The study of this body produced these difficulties, that according to the conditions of the reaction, compounds were obtained which, although of the same composition, yet a had different chemical behaviour. If the assumed hydroxy-oxime is treated with weak acids (oxalic acid), an aldehyde is obtained, but when stronger acids are used (sulphuric acid) a ketone results. The aldehyde $C_{10}H_{14}O_2$ is regenerated with oxalic acid from its semicarbazone (m.p. 209°), and boils at 96° (11 mm. pressure); d 0,97; $n_{D19°}$ 1,4952. The aldehydic character of the body $C_{10}H_{14}O$ was shown by the formation of an acid $C_{10}H_{14}O_2$ when it was heated with silver solution. This is the first synthesis of an aldehyde of the terpene-series through a nitrosyl chloride addition, product. The ketone regenerated (with sulphuric acid 1 in 2) from the semicarbazone had a menthone-like odour, and the boiling point 93° (13 mm. pressure), 218 to 220° at atmospheric pressure; d 1,001; $n_{D20°}$ 1,4937. The compound is isomeric with carvone; the high specific gravity is striking, for a ketone heavier than water has not yet been observed in the terpene-series. The ketone is unsaturated. Wallach explains the formation of the ketone by the occurrence of atomic or linking-displacements, not by the fact that the aldehyde is perhaps formed in the first instance, which would be the most obvious. With regard

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[1]) Liebig's Annalen **345** (1906), 127.
[2]) Liebig's Annalen **324** (1902), 79; Report October **1902**, 93; comp. also Report April **1901**, 74.

to the character of the ketone, in view of the high specific gravity it does not appear to be a question of the as yet unknown menthocarvone, but probably of a representative of the bicyclic system.

Citronellol. The reduction of unsaturated primary fatty alcohols by ammonium metals[1]) was also applied by E. Chablay[2]) to citronellol, from which a pleasantly smelling hydrocarbon was obtained which had the following constants: b. p. 168 to 169° (ordinary pressure): $d_{15°}$ 0,789; $d_{22,5°}$ 0,777; $n_{D22,6°}$ 1,4484. Elementary analysis showed 85,47 and 85,62 % C, 13,37 and 13,40 % H; calculated for $C_{10}H_{20}$ (dimethyl-2-6-octene-2) 85,72 % C and 14,28 % H. The author attributes the slight differences to imperfect purity, but does not doubt that the body obtained actually represents dimethyl-2-6-octene-2, and possesses the following formula corresponding to the citronellol formula: —

$$CH_3 - C(CH_3) = CH - CH_2 - CH_2 - CH(CH_3) - CH_2 - CH_3$$

Nerol. We have already[3]) briefly referred to the properties of the pure nerol produced by v. Soden and Treff. The method of production recently followed by the above-mentioned authors[4]), is as follows: a mixture of diphenyl urethanes produced from nerol containing geraniol, can readily be split up by fractional crystallisation in suitable solvents (petroleum ether, methyl alcohol), owing to the differences in solubility. The alcohols are then regenerated from the pure urethanes by saponification, and purified in the usual manner. The crude material was crude nerol produced from petitgrain oil, which no longer reacted with calcium chloride. Nerol, which as is well known absorbs 4 atoms bromine, yields with bromine a finely crystallising tetrabromide of the m. p. 118 to 119°. The results of the oxidation of nerol do not allow definite conclusions to be drawn with regard to its constitution. The authors assume that with careful oxidation citral a, the aldehyde which chiefly occurs when oxidising geraniol, is only formed in small quantities, and that with chromic acid there is formed either principally citral b, or a new aldehyde which, however, hardly differs at all in the odour from the two former; with regard to the occurrence of the two citrals, this would point to atomic transposition. It should still be mentioned that v. Soden and Treff have also succeeded in producing a solid geraniol tetrabromide, by allowing 4 parts by atomic weight of bromine to act on geraniol dissolved in cold chloroform. The oily bromide was left standing for several weeks in

[1]) Compt. rend. **140** (1905), 1343, 1396.
[2]) Ibidem **143** (1906), 123.
[3]) Repor April **1904**, 109.
[4]) Berl. Bᵗerichte **39** (1906), 906.

the desiccator, and it finally separated off small needles in wart-like groups (m. p. 70 to 71°), which readily dissolve in ether, but with difficulty in petroleum ether. By inoculation with a crystal of the solid bromide, the authors then obtained from the oily product almost quantitatively the solid tetrabromide. They are of opinion that in the analysis of essential oils, more attention should in future be paid to nerol as a constituent, as the number of oils containing nerol is presumably large.

Now while v. Soden and Treff only deal with constitutional questions in so far, as to seek the difference between the two extremely similar bodies nerol and geraniol in a displacement of the double linking $\cdot \underset{CH_3}{C} :$ present in geraniol in the two possible directions: —

$$C_3H_5 \cdot [CH_2]_3 \cdot CH : \underset{CH_3}{\underset{\cdot}{C}} \cdot C_2H_4 \cdot OH \quad \text{and} \quad C_3H_5 \cdot [CH_2]_2 \cdot CH_2 \cdot \underset{CH_2}{\underset{\cdot\cdot}{C}} \cdot C_2H_4 \cdot OH$$

a work by O. Zeitschel[1]) occupies itself with the constitution of nerol as well as with its production from linalool. Based upon older work by Barbier[2]), Bouchardat[3]), Bertram and Gildemeister[4]), and also Stephan[5]), a new examination of the products resulting from the action of acetic anhydride on linalool proved the fact, which had escaped the earlier investigators, that the latter, as well as geraniol and terpineol, is also isomerised into nerol. Contrary to v. Soden's and Treff's view mentioned above, and the same opinion held by Semmler, Zeitschel believes that the difference between geraniol and nerol is caused by different spatial arrangements in the sense of geometrical isomerism with regard to the double-linking which is nearest to the hydroxyl-group in the end-position. The following graphic formulæ correspond to Tiemann-Semmler's geraniol formula for the two stereo-isomeric citrals: —

$$\begin{array}{ll} \text{I.} & \text{II.} \\ CH_3 \cdot \underset{\cdot\cdot}{C} \cdot CH_2 \cdot CH_2 \cdot CH : C(CH_3)_2 & CH_3 \cdot \underset{\cdot\cdot}{C} \cdot CH_2 \cdot CH_2 \cdot CH : C(CH_3)_2 \\ CHO \cdot C \cdot H & H \cdot C \cdot CHO \\ \text{(citral a = geranial)} & \text{(citral b = neral)} \end{array}$$

and for the two corresponding stereo-isomeric alcohols: —

$$\begin{array}{ll} \text{III.} & \text{IV.} \\ CH_3 \cdot \underset{\cdot\cdot}{C} \cdot (CH_2)_2 \cdot CH : C(CH_3)_2 & CH_3 \cdot \underset{\cdot\cdot}{C} \cdot (CH_2)_2 \cdot CH : C(CH_3)_2 \\ CH_2(OH) \cdot C \cdot H & H \cdot C \cdot CH_2OH \\ \text{(geraniol)} & \text{(nerol)} \end{array}$$

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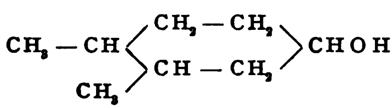
1) Berl. Berichte **39** (1906), 1780.
2) Compt. rend. **116** (1893), 1200.
3) Ibidem, 1253.
4) Journ. f. prakt. Chem. II. **49** (1904), 192; **53** (1896), 225.
5) Journ. f. prakt. Chem. II. **58** (1898), 109.

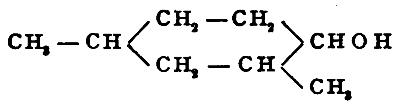
As the reduction of citral to nerol, but also the oxidation of nerol to citral was carried out successfully, Zeitschel concludes, on the presumption that no other structure-isomeric citral is detected in lemongrass oil in any appreciable quantity, that either formula III, or formula IV belongs to nerol. According to Tiemann and Schmidt, namely, linalool can be much more readily converted into terpin hydrate by shaking with dilute sulphuric acid than geraniol; Zeitschel finds for the rapidity of the terpin-hydrate-formation the relative proportion 1 (ger.) : 5 (lin.) : 9 (ner.), and this rapid conversion of nerol in terpin hydrate, contrary to the slow behaviour of geraniol, induces the author to accept for nerol formula IV, for geraniol formula III, by means of which the opposite spatial arrangements of the two alcohols are most naturally explained; nerol would accordingly by stereo-isomeric with geraniol, citral b identical with neral, citral a with geranial.

H. v. Soden and W. Treff[1]) found in their comparative examinations that artificial and natural nerol are absolutely identical.

Cyclohexanol. If 1,2,4-, 1,3,4-, or 1,4,2-xylenol is passed over reduced nickel in the presence of an excess of hydrogen, there are obtained, according to P. Sabatier and A. Mailhe[2]), the three corresponding dimethylcyclohexanols. The conditions of the reaction are, however, not the same in the three cases. 1,2,4-xylenol passes over for two thirds into o-xylene boiling at 141°, whilst the remaining third does not consist of pure dimethyl-1,2-cyclohexanol-4, but 25% of it represent the corresponding ketone. The alcohol



has the odour of cyclohexanol; b. p. 189° (corr.); $d\frac{0^\circ}{4^\circ}$ 0,9261; $d\frac{16^\circ}{4^\circ}$ 0,9073; n_{D16° 1,458; the phenyl urethane melts at 119°; by oxidation with chromic acid mixture or by abstraction of hydrogen over copper, there is formed from the alcohol the ketone, b. p. 187°, whose badly crystallising semicarbazone melts with decomposition at 175°. — 1,3,4-xylenol yields, in addition to dimethyl-1,3-cyclohexanol-4,



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[1]) Berl. Berichte **39** (1906), 1792.
[2]) Compt. rend. **142** (1906), 553; comp. also Report October **1905**, 101.

(b. p. 176,5° [corr.]; $d_{4^\circ}^{0^\circ}$ 0,9235; $d_{4^\circ}^{16^\circ}$ 0,9119; n_{D16° 1,458), but little ketone and m-xylene. The phenyl urethane melts at 96°, the acetic ester boils at 198° (corr.). By the action of molten zinc chloride the alcohol is converted into a hydrocarbon which appears to be identical with a hydrocarbon which the authors have previously[1]) obtained from dimethyl-1,3-cyclohexanol-3, viz., dimethyl-1,3-cyclohexene-4, b. p. 124°; $d_{4^\circ}^{0^\circ}$ 0,8210; n_D 1,451. On oxidation with chromic acid mixture or abstraction of hydrogen over copper, there is formed from the alcohol, dimethyl-1,3-cyclohexanone-4 (b. p. 176,5° [corr.]; $d_{4^\circ}^{0^\circ}$ 0,9210; $d_{4^\circ}^{16^\circ}$ 0,9124; n_{D16° 1,446), whose semicarbazone melts at 190° with decomposition. 1,4,2-xylenol yields, in addition to 90 % alcohol, 10 % ketone without formation of xylene. Dimethyl-1,4-cyclohexanol-2 (b. p. 178,5° [corr.]; $d_{4^\circ}^{0^\circ}$ 0,9218; $d_{4^\circ}^{16^\circ}$ 0,9073; n_{D16° 1,455) yields a phenyl urethane of the m. p. 115°. Dimethyl-1,4-cyclohexanone-2 boils at 176° (corr.); its semicarbazone melts at 155° with decomposition.

Aldehydes.

G. Darzens and P. Lefébure[2]) have applied Darzens' synthesis of glycide esters to cyclohexanones, and produced by decomposition of the corresponding glycidic acids the relative hexahydrobenzaldehydes. If to a mixture of equal molecules cyclohexanone and monochloracetic ester at 0°, 1 mol. dry sodium ethylate is slowly added, the mixture left standing first of all at ordinary temperature for 48 hours, then for 6 hours on a water bath, and the condensation-product dissolved in water, there is obtained in a yield of 65 %, the glycide ester of cyclohexylacetic acid of the formula

$$CH_2\left\langle\begin{matrix} CH_2-CH_2 \\ CH_2-CH_2 \end{matrix}\right\rangle \underset{\diagdown_{O}\diagup}{C - CH} - COOC_2H_5.$$

The ester boils at 128 to 129° (17 mm. pressure), has a faint skatol-like odour, and can be very readily saponified. In order to produce hexahydrobenzaldehyde, the free acid is slowly distilled *in vacuo* (30 mm. pressure), when it is split up into aldehyde and carbon dioxide. The aldehyde boils at atmospheric pressure between 155 and 157°, at 20 mm. between 75 and 78°. It has a very strong odour of valeric aldehyde; its semicarbazone melts at 173 to 174°. From o-methylcyclohexanone is formed in an analogous manner o-methylhexahydrobenzaldehyde, a body not yet known; b. p. 61 to 62°

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1) Ibidem **141** (1905), 21.
2) Compt. rend. **142** (1906), 714.

(15 mm. pressure). Its odour is powerful and reminds of camphor; m. p. of the semicarbazone 137 to 138°. In the same manner were formed m-methylhexahydrobenzaldehyde from m-methylcyclohexanone; and p-methylhexahydrobenzaldehyde from p-methylcyclohexanone. This method is said to give good yields.

Citronellal. If, according to A. Klages and R. Sautter[1]), by the action of bromobenzene magnesium on citronellal the benzene nucleus is introduced into the asymmetric molecule of citronellal, the fatty-aromatic carbinol formed can be converted by suitable operations in active dimethooctylbenzene, $(CH_3)_2 : CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot C_6H_5$. An interesting insight is thereby obtained in the changes of the rotatory power of the substances.

Ketones.

Carvone. According to Goldschmidt and Kisser[2]), the treatment of carvoxime hydrochloride or hydrobromide with alcoholic alkali leads to the so-called isocarvoxime (m. p. 142 to 143°), which according to its constitution must be regarded as the oxime of a carvone-isomeric with regard to the position of the double linkings. When isocarvoxime is heated with dilute sulphuric acid, there is formed, besides carvacrol, a basic compound melting at 94°, also isomeric with carvoxime, which was designated by Goldschmidt[3]) as "carvoline", and was regarded as the product of a Beckmann's transposition. Wallach[4]) has now obtained abundant quantities of carvoline (40%) both by heating isocarvoxime with dilute mineral acids, and by boiling with aqueous oxalic acid, that is to say under conditions, under which a genuine Beckmann's re-arrangement has not yet been observed. The isocarvoxime used as crude material, m. p. 143 to 144°, b. p. 157 to 159° (12 mm. pressure) which regenerates carvoxime hydrochloride by absorption of hydrochloric acid, was identified by its dibromide (m. p. 126 to 127°), better by its tetrabromide (m. p. 134 to 135°). From the isocarvoxime the carvoline was then produced by heating with dilute sulphuric acid; it melts at 94° (its hydrochloride at 189 to 190°), and boils at 12 mm. at 158 to 163°, at ordinary pressure at 289 to 290° (not corr.). The base is isomeric with carvoxime, and represents a primary aromatic hydroxy base. The aromatic amido-character appears from the diazotising. The oxygen is present in the form of hydroxyl,

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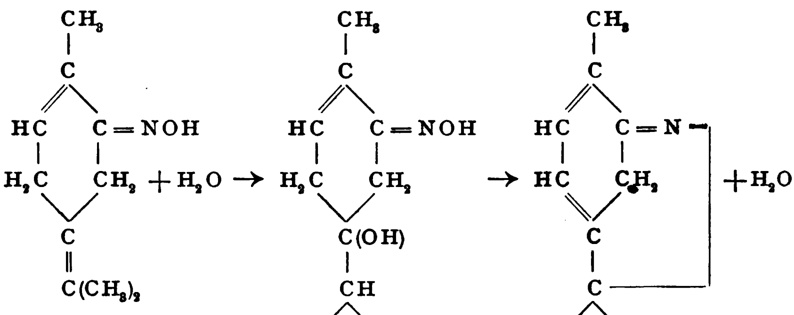
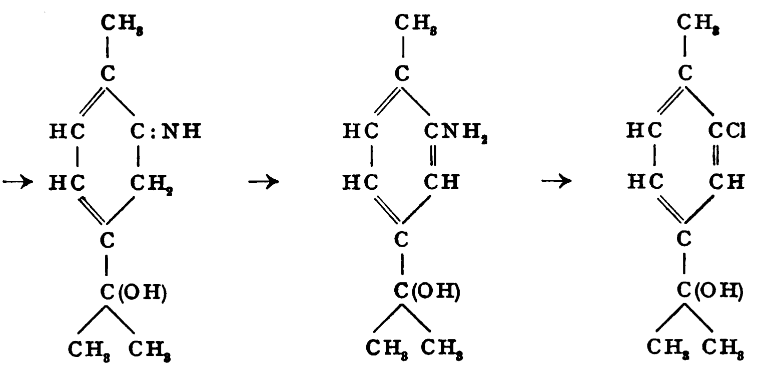
[1]) Berl. Berichte **39** (1906), 1938.
[2]) Berl. Berichte **20** (1887), 2073; **22** (1889), 3104; **26** (1893), 2085.
[3]) Ibidem **29** (1896), 12.
[4]) Liebig's Annalen **346** (1906), 266.

but not in the nucleus, for the compound is insoluble in alkali. But the hydroxyl can be replaced on boiling with hydriodic acid by hydrogen, whereby carvacrylamine is formed. Carvoline is therefore a derivative of p-cymene, which has the amido-group in o-position to the methyl. Diazotised carvoline can be combined with phenols to form dyes. The amido-group can be substituted by chlorine, whereby an hydroxychloride (m. p. 50 to 51°) is formed boiling without decomposition between 245 and 249°. With chromic acid mixture it is oxidised to p-acetyl-o-chlorotoluene passing over with water vapour, melting at 45 to 46°, and boiling at 250 to 254°. This body has a distinct ketonic character; its semicarbazone melts at 237 to 238°, its oxime at 96 to 97°. The ketone could be converted by oxidation with hypobromite into an acid melting at 200 to 201°, which therefore showed the melting point of o-chloro-p-toluic acid. The following graphic formulæ represent all the reactions described: —

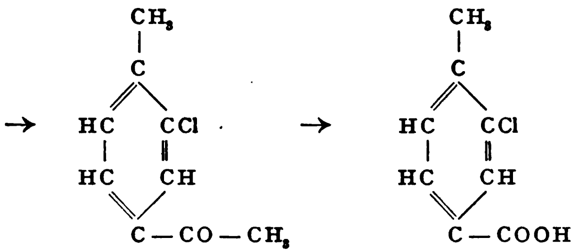


isocarvoxime



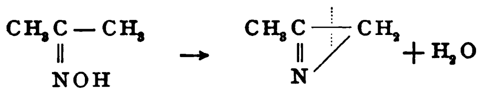
carvoline (hydroxycarvacrylamine)

hydroxychloride



o-chloro-p-acetyltoluene o-chloro-p-toluic acid

The mechanism of the change from isocarvoxime to carvoline is now no longer explained by Wallach by accepting a Beckmann's re-arrangement; on the contrary, he rather considers the first-named reaction an explanation of the latter. For the mutual exchange of the radicals CH_3 and OH would for example fail in the case of cyclic oximes, if the exchange of radicals is not taken as purely schematic. But if, on the other hand, the intermediary formation of a nitrogenous ring is considered as the first phase of the reaction:



acetoxime

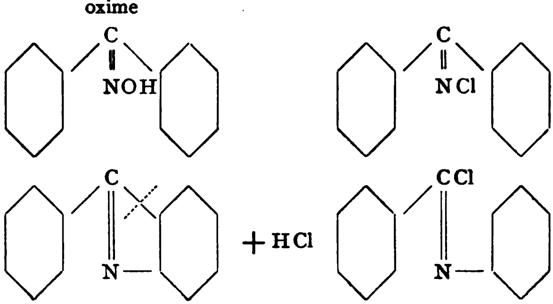
which in the second phase is again opened in another direction, forming now a more stable system:

$$\begin{array}{c} CH_3COH \\ \| \\ N \cdot CH_3 \end{array} \longrightarrow \begin{array}{c} CH_3CO \\ \| \\ NHCH_3 \end{array}$$

methylacetamide

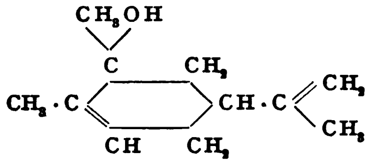
the interpretation of all the changes is entirely uniform. In the presence of only aromatic radicals, the re-arrangement by means of phosphorus chloride is explained by the following graphic formulæ

oxime

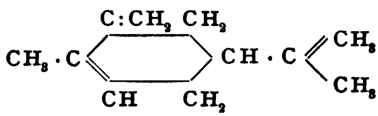


imide chloride.

H. Rupe has continued his researches as to the knowledge of carvone, to which we have already referred once before[1]). Conjointly with K. Liechtenhan he publishes a further communication[2]). When treating carvone with methylmagnesium iodide there should be produced, analogous to the experiments with dihydrocarveol, methylcarveol:



in order to arrive from this, by adding water, etc., to methylpinol. But instead of this, there was formed from carvone, with Grignard's salts, not an alcohol, but a hydrocarbon distilling between 68 and 80°, chiefly at 74 to 75° (10 mm. pressure), or at 195 to 197° (745,5 mm. pressure); it represents a water-white liquid with a pleasant odour reminding of cajeput oil and limonene, and has the formula $C_{11}H_{16}$ (d_{20° 0,8726; n_{D20° 1,5007; $[\alpha]_{D20^\circ}$ + 70,38°). Of the three possible formulæ most probably the hydrocarbon possesses the following: —



One fact speaks particularly in favour of this formula. If, namely, the hydrocarbon is reduced with sodium and amyl alcohol, there is formed, according to Rupe, a dihydro derivative (b. p. 72 to 74° at 9,5 mm. pressure). The lowering of the rotatory power thereby observed is explained by the occurrence of a new asymmetric carbon atom. In addition to the above-mentioned crude hydrocarbon, a small quantity of a ketone was formed, methyl dihydrocarvone, of which the oxime was isolated partly in solid and partly in liquid form. The liquid oxime boils at 141 to 145° (11 mm. pressure). The ketone regenerated from the oxime or the semicarbazone by boiling with sulphuric acid, passed over chiefly at 102 to 103,5° (11 mm. pressure). Further examinations must show whether it is here perhaps a question of two isomerides.

Whilst dihydrocarvone is converted into carvenone, according to Wallach, by boiling with dilute, and according to v. Baeyer by treatment with concentrated sulphuric acid, this conversion, according to Rupe and Liechtenhan, does not take place when dihydro-

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1) Berl. Berichte **38** (1905), 1719; Report October **1905**, 112.
2) Berl. Berichte **39** (1906), 1119.

carvone is shaken with 40 per cent. sulphuric acid. On the contrary, by addition of water there is formed 8-hydroxytetrahydrocarvone:

$$CH_3\cdot C\left\langle\begin{matrix}CO-CH_2\\CH_2-CH_2\end{matrix}\right\rangle CH\cdot C(OH)\left\langle\begin{matrix}CH_3\\CH_3\end{matrix}\right.$$

a body which Knoevenagel and Samel[1]) had already obtained by another method. Its oxime melts at 120 to 121°, the semicarbazone, recrystallised from methyl alcohol, at 157 to 158°. When 8-hydroxytetrahydrocarvone is boiled, carvenone is formed. On reduction of 8-hydroxytetrahydrocarvone the α-compound of 2,8-dioxyterpane (m. p. 112 to 113°) is formed, and this fact confirms the constitution of the former.

In a third communication Rupe describes, jointly with Dorschky[2]), the two semicarbazones of carvone. The first (m. p. 141 to 142°) obtained also by Knoevenagel and Samel[3]) is only formed if carvone, alcohol, and potassium acetate are added to a concentrated aqueous solution of semicarbazide hydrochloride, and an increase of temperature is avoided. Without this precaution, and if sodium bicarbonate is used instead of potassium acetate, the second semicarbazone (m. p. 162 to 163°) of v. Baeyer is formed. The lower melting one is more labile, and already passes over into the other form when simply left standing. The constants of the two bodies are as follows: carvone semicarbazone of the m. p. 141 to 142°: $[\alpha]_{D20^\circ}$ $+$ 11,30° (in pyridine); carvone semicarbazone of the m. p. 162°: $[\alpha]_{D20^\circ}$ $+$ 11,50° (in pyridine).

In connection with the work of Rupe and Liechtenhan quoted above, A. Klages[4]) states that he also, independent of the above-mentioned authors, in conjunction with F. Sommer has succeeded in producing in a good yield, from carvone and bromomethyl magnesium, the hydrocarbon $C_{11}H_{16}$, and also the 2-methylcarveol which Rupe and Liechtenhan had been looking for. As the hydrocarbon could be converted into 2-methyl cymene, Klages gives it the formula of a 2-methyl-$\Delta_{2,6,8(9)}$-menthatriene, and not the formula of a methene hydrocarbon drawn up by Rupe and Liechtenhan. The conversion succeeds best by boiling the methyl menthatriene with a mixture of 2 per cent. glacial acetic acid and hydrochloric acid. 2-Methylcarveol (2-methyl-$\Delta_{6,8(9)}$-menthadienol), $d\frac{20,4^\circ}{4^\circ}$ 0,9471; $n_{D20,4^\circ}$ 1,4911; $\alpha_{D20,4^\circ}$ $+37,17^\circ$; $[\alpha]_{D20,4^\circ}$ $+36,08^\circ$; b. p. 111° (14 mm. pressure). 2-Methyl-$\Delta_{2,6,8(9)}$-menthatriene: $d\frac{21,1^\circ}{4^\circ}$ 0,8724; $n_{D21,1^\circ}$ 1,5000; α_{D21° $+60,30^\circ$; $[\alpha]_{D21^\circ}$ $+69,21^\circ$; b. p. 82 to 83° (15 mm. pressure). 2-Methyl-p-cymene:

[1]) Berl. Berichte **39** (1906), 677; Report April **1906**, 122.
[2]) Berl. Berichte **39** (1906), 2112.
[3]) Ibidem **39** (1906), 681.
[4]) Berl. Berichte **39** (1906), 2306.

$d\frac{21,1^\circ}{4^\circ}$ 0,8729; $n_{D21,1^\circ}$ 1,4991; b. p. 86 to 87,5° (16 mm. pressure), 198° (732 mm. pressure). In an analogous manner is also formed 2-ethyl-p-cymene from 2-ethyl-$\Delta_{2,6,8(9)}$-menthatriene. 2-Ethylcarveol: $d\frac{21^\circ}{4^\circ}$ 0,9302; $[\alpha]_{D21^\circ}$ + 31,17°; n_{D21° 1,4879; b. p. 118,5 to 119,5° (14 mm. pressure). 2-Ethyl-$\Delta_{2,6,8(9)}$-menthatriene: $d\frac{18^\circ}{4^\circ}$ 0,8859; $[\alpha]_{D18^\circ}$ + 86,19°; n_{D18° 1,5041; b. p. 100 to 101° (13,5 mm. pressure). 2-Ethyl-p-cymene: $d\frac{21,1^\circ}{4^\circ}$ 0,8665; $n_{D21,1^\circ}$ 1,4965; b. p. 103° (19 mm. pressure). This conversion into the benzene hydrocarbon is most easily accomplished with 2-phenyl carveol; in this case, even the 2-phenyl menthatriene was not obtained in the pure state. 2-Phenyl-carveol: $d\frac{15,1^\circ}{4^\circ}$ 1,0156; $[\alpha]_{D15,1^\circ}$ + 81,42°; $n_{D15,1^\circ}$ 1,5562. The crude oil boiled at 145 to 168° (12 mm. pressure), the bulk at 159 to 160°. 2-Phenyl-$\Delta_{2,6,8(9)}$-menthatriene: highest rotation observed + 110,2° (13,8°); $d\frac{13,8^\circ}{4^\circ}$ 0,9882; $n_{D13,8^\circ}$ 1,5631; b. p. 152 to 153° (13 mm. pressure). 2-Phenyl-p-cymene: $d\frac{13,8^\circ}{4^\circ}$ 0,9822; α_{D15° ± 0°; $n_{D13,8^\circ}$ 1,5670; b. p. 153 to 154° (14 mm. pressure).

V. J. Nikitine[1]) has produced some new terpene alcohols derived from carvone and dihydrocarvone respectively. If, according to v. Baeyer, alcoholic potash is allowed to act on the hydrobromide of dihydrocarvone in a freezing mixture, carone is formed, and from the latter, by treatment with sodium in ethereal solution, an alcohol $C_{10}H_{20}O$ (b. p. 103° [12 mm. pressure], n_D 1,4651, $d\frac{23^\circ}{4^\circ}$ 0,9086; $[\alpha]_D$ 24,36°), which can be converted into caromenthane. By the action of methylmagnesium iodide there is formed from carvone an alcohol $C_{11}H_{20}O$, b. p. 99 to 101° (13 mm. pressure); and when dihydrocarvone is reduced with sodium and alcohol, there results an alcohol $C_{10}H_{18}O$ (b. p. 107 to 108° [17 to 18 mm. pressure], 220° [ord. pressure], $d_{19,5^\circ}$ 0,9224, n_D 1,4773, $[\alpha]_D$ + 22,9°), which is therefore, according to its constants, not identical with Wallach's dihydrocarveol.

If molecular quantities of hydrocyanic acid and carvone are allowed to act on each other[2]), there is formed cyanodihydrocarvone (m. p. 93,5 to 94,5°; $[\alpha]_D$ + 13,5° in alcoholic solution):

$$CH_3 \cdot CH \left\langle \begin{array}{l} CO \text{———} CH_2 \\ CH(CN) \cdot CH_2 \end{array} \right\rangle CH \cdot C \begin{array}{l} /\!\!/ CH_2 \\ \diagdown CH_3 \end{array}$$

[1]) Journ. russ. phys.-chem. Ges. **36**, 780.
[2]) Proceed. Chem. Soc. **20** (1904), 54.

(semicarbazone, m. p. 224°; oxime, m. p. 169 to 170°; α-cyanodihydrocarvone dibromide, $[\alpha]_{D18^\circ}$ in alcoholic solution + 29,0°; m. p. 146 to 147°; β-cyanodihydrocarvone dibromide, $[\alpha]_{D18^\circ}$ in alcoholic solution + 6,0°; m. p. 91 to 92°; chlorocyanodipentene [by the action of phosphorus pentachloride and heating the reaction-product with quinoline], $C_{11}H_{14}NCl$, b. p. 268 to 270° [ord. pressure]). By hydrolysing cyanodihydrocarvone there are formed, according to A. Lapworth[1]), two stereo-isomeric carboxylic acids:

$$CH_3 \cdot CH \left\langle \begin{array}{l} CO \text{———} CH_2 \\ CH(COOH) \cdot CH_2 \end{array} \right\rangle CH \cdot C \left\langle \begin{array}{l} CH_2 \\ CH_3 \end{array} \right.$$

The α-acid, m. p. 97 to 98°, predominates when the hydrolysis is incomplete; it can best be purified by recrystallisation from ethyl formiate; $[\alpha]_D$ + 49,9° (in ethyl acetate). This acid has the properties of an unsaturated keto acid, its semicarbazone becomes brown at 210°, and melts with decomposition at 218 to 221°; the oxime softens at 180°, then becomes brown, and melts with evolution of gas at 193 to 194°. — The β-acid which is formed on complete hydrolysis, melts at 142 to 143°; $[\alpha]_D$ + 28,8° (in ethyl acetate); its semicarbazone melts with decomposition at 235 to 236°. — The oxidation of both acids in ice-cold soda solution with 1 per cent. permanganate yields a compound of the gross formula $C_{11}H_{16}O_4$; m. p. 149 to 151°. From the neutralised β-keto acid and hydrocyanic acid, there originated a cyanohydrin $COOH \cdot C_{10}H_{15}(OH)CN$, m. p. 188 to 190°. Finally the mutual conversibility of the two isomeric dihydrocarvone carboxylic acids was etablished.

Camphor. We have before us a communication from O. Schmidt[2]) on the synthetic preparation of camphor from oil of turpentine, a subject which we have repeatedly referred to in our Reports[3]). The author produced camphor on the one hand from solid pinene hydrochloride by conversion of the latter into camphene, esterification and saponification of the camphene to isobornyl ester or isoborneol, and oxidation of the latter to camphor. On the other hand he boiled turpentine oil with o-chlorobenzoic acid (in a manner analogous to v. Heyden's withdrawn German patent application). The first method gave a yield of camphor of 24,4 % = 21,9 % theoretically, the second method yielded 28 % = 25,1 % theoretically. Of terpenes there were regenerated 42,3 and 53,0 % respectively. Whether the losses, which occur when such small quantities as 100 g. turpentine oil are worked off, can be avoided, is a matter which requires confirmation. Owing

[1]) Journ. chem. Soc. **89** (1906), 945.
[2]) Chem. Ind. **29** (1906), 241.
[3]) Reports April **1903**, 15, 85; October **1904**, 123; April **1905**, 117.

to the other difficulties of the production of synthetic camphor on a large scale, which are specially due to the great cost of the crude material, it remains questionable whether synthetic camphor will be able to compete permanently with the natural product.

A. Haller and J. Minguin[1]) have examined the products resulting from the action of sodium isobutylate and propylate on camphor at high temperatures. When heated for 24 hours in an autoclave to 220 to 230°, a butter-like reaction-product is formed, from which water dissolves sodium isobutylate, ether dissolves an oil. The latter when submitted to fractional distillation yielded isobutyl alcohol, borneol ("camphol"), and a syrupy oil of the b. p. 235 to 255°, from which on cooling to about 0° after some days isobutyl borneol, $C_{14}H_{26}O$ could be separated off; m. p. 55°; $[\alpha]_D + 20°7'$ in alcoholic solution; acetylation yielded an ester of the b. p. 135° (20 mm. pressure) from which after saponification the original oil was regenerated. Isobutyl borneol

$$C_8H_{14}\left\langle\begin{array}{l} CH \cdot CH_2 \cdot CH\left\langle\begin{array}{l}CH_3\\CH_3\end{array}\right. \\ | \\ CH \cdot OH \end{array}\right.$$

is not attacked in acetone solution by permanganate in the cold, but in benzene solution it is converted, by shaking for 12 hours with a sulphuric acid solution of permanganate, into isobutyl camphor (m. p. 28°; $[\alpha]_D$ in alcoholic solution $+ 72°4'$), which after heating in a tube to 100° with equimolecular quantities bromine and treating the reaction-product with alcoholic potash, yields isobutylidene camphor

$$C_8H_{14}\left\langle\begin{array}{l} C : CH \cdot CH(CH_3)_2 \\ | \\ CO \end{array}\right.$$

b. p. 145° (10 mm. pressure); $[\alpha]_D + 114°4'$. The latter is converted by the action of concentrated nitric acid, or of amylnitrite and nitric acid, into its nitrosate; m. p. 178° with decomposition; $[\alpha]_D$ (acetone solution) $+ 93°$. With dilute potash liquor the nitrosate is converted into isonitroso isobutyl oxycamphor,

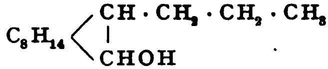
$$C_8H_{14}\left\langle\begin{array}{l} COH \cdot \overset{NOH}{\ddot{C}} \cdot C_3H_7 \\ | \\ CO \end{array}\right.$$

m. p. 85°. If sodium isobutylate is allowed to act under normal pressure at the reflux condenser on camphor, the same reaction takes place, only that as principal product isobutylidene camphor is formed

[1]) Compt. rend. **142** (1906), 1309.

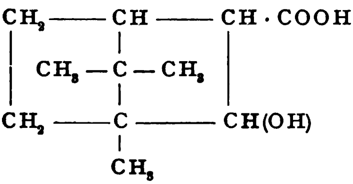
in addition to a small quantity of isobutyl borneol. Sodium propylate gives analogous derivatives, although in smaller yield.

Propyl borneol

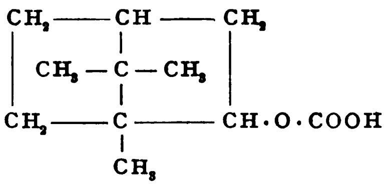


m. p. 61°; $[\alpha]_D + 12° 5'$ in methyl alcohol. The liquid propyl camphor boils at 123° (14 mm. pressure), $[\alpha]_D + 55° 6'$. Propylidene camphor could not be obtained in the pure state; the liquid obtained showed a rotatory power of $+ 87° 6'$. The nitrosate melted with decomposition at 160°.

Jointly with K. Burkheiser, J. Bredt[1]) has worked on the electro-reduction of camphocarboxylic acid to borneol carboxylic acid, and on dehydroborneol carboxylic acid. The electric current reduced the camphocarboxylic acid easily and almost completely in potash solution with a potassium amalgam cathode. (E. M. F. 30 volts, current 7 to 7,5 amperes, temperature about 30°.) In this electro-reduction camphocarboxylic acid absorbs two hydrogen atoms, with formation of a β-oxycamphane carboxylic acid (m. p. 170 to 171°). The last-named acid, which Bredt for the present, under reserve, addresses as borneol carboxylic acid, is isomeric with the very unstable borneol carbonic acid (carbonic acid mono bornyl ester) produced by Baubigny[2]): —



borneol carboxylic acid



borneol carbonic acid
(carbonic acid mono bornyl ester)

The analysis of the calcium salt, calculated for an acid $C_{11} H_{18} O_3$, gave results which agree very well. A second acid formed in the reduction was identified with certainty as an isomeride of borneol carboxylic acid, m. p. 101 to 102°. If the borneol carboxylic acid of the m. p. 170 to 171° is repeatedly slowly distilled *in vacuo* (13 mm. pressure), there is obtained between 160 and 170°, dehydroborneol carboxylic acid (camphene carboxylic acid?) which, contrary to the first-named, is volatile with water vapour, and can thereby be separated from it; it melts at 112 to 113° and has the formula $C_{11} H_{16} O_2$. Its calcium salt crystallises from water, the silver salt dissolves with difficulty, and

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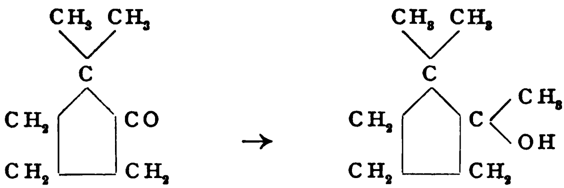
1) Liebig's Annalen **348** (1906), 199.

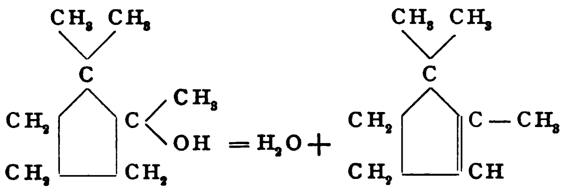
2) Zeitschr. f. Chemie **1868**, 299.

keeps fairly well in the light. The camphyl glycol produced by the Farbwerke vorm. Meister Lucius & Brüning[1]), which consists of two stereo-isomeric glycols, cis- and trans-glycol, shows, according to Bredt, a very near relationship to the borneol carboxylic acids described. Dehydrocamphyl carbinol formed from cis- and trans-camphyl glycol by heating or treatment with mineral acids, corresponds to all appearances in its constitution with camphene carboxylic acid; it is moreover, like the latter, volatile with water vapour.

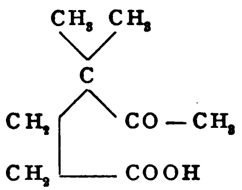
The synthesis of isolaurolene and isolauronolic acid has long been known in principle, but it has found practical application only in the synthesis of α,α-substituted dimethyladipic acid. G. Blanc[2]) converted it, by heating with acetic anhydride, into its anhydride, from which is formed by slow distillation at ordinary pressure dimethylcyclopentanone, and from the latter by condensation with methylmagnesium iodide a tertiary alcohol:



which on distillation at ordinary pressure is split up into water and a hydrocarbon identical with isolaurolene:



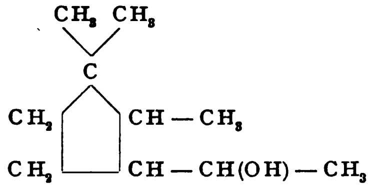
This hydrocarbon is exidised with potassium permanganate to dimethylpentanone carboxylic acid (m. p. 48°)



[1]) German Patent 123909; Friedländer, Fortschritte der Teerfarbenfabrikation und verwandter Industriezweige VI., p. 1268.

[2]) Compt. rend. **142** (1906), 1084.

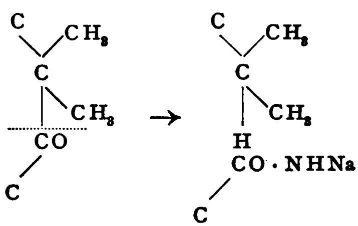
The action of aluminium chloride and acetyl chloride on isolaurolene produces a ketone, and reduction with sodium and alcohol from the latter the secondary alcohol



which on oxidation with nitric acid yields dihydroisolauronolic acid, and by brominating the hydrogen atom in the α-position, and loss of hydrobromic acid, yields isolauronolic acid.

As to the conditions regarding the dynamic isomerism in camphor derivatives, see under Physical notes, p. 105.

Fenchone. As already mentioned by us in our last Report[1]), various reactions of fenchone and camphenilone had induced F. W. Semmler to draw up for the former a formula which differs from the otherwise generally accepted formula of Wallach. From Semmler's formula, fenchone appears as a methylated camphenilone, whilst according to Wallach camphor and fenchone differ solely in the position of the methyl groups. Semmler[2]) sees in the products of decomposition of fenchone fresh evidence for his view. A reagent which has a closer relationship to the CO-group, and consequently splits up the molecule at the keto-group, was found by his recent researches in sodium amide. Cyclic ketones which, like fenchone, possess next the keto-group a dimethylated carbon atom, suffer by the action of sodium amide a ring-disruption, with formation of the sodium amide of the corresponding acid: —



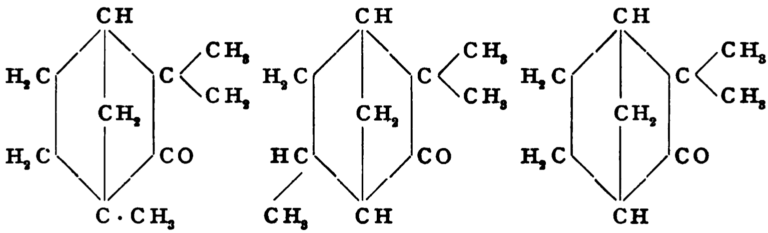
Dihydrofencholenic acid amide, $C_{10}H_{19}ON$, is formed by the action of molecular quantities sodium amide on fenchone in benzene solution

[1]) Chem.-Ztg. **29** (1905), 1313; Report April **1906**, 124.
[2]) Berl. Berichte **39** (1906), 2577.

(m. p. 94°; b. p. 160° [11 mm. pressure]; α_D in 25 per cent. ethereal solution $+1°$). Contrary to the dihydrofencholenic acid amide (a) (m. p. 130,5°) of Mahla[1]), Semmler designates his as (b). By saponifying the amide with alcoholic potash liquor, the corresponding dihydrofencholenic acid (b), (b. p. 140 to 141° [10 mm. pressure]; $d_{15°}$ 0,9742; n_D 1,45862; $\alpha_D +3°12'$) is formed. The acid yields a whole series of characteristic reaction-products. On the strength of the acceptance of a dimethylated carbon-atom in fenchone next to the keto-group, and of the peculiar disruption of the one 5-ring in fenchone, caused by this constitutional character, Semmler accepts for camphenilone an analogous disruption, provided that in the latter the carbonyl-group has also next to it a dimethylated carbon-atom. From camphenilone, $C_9H_{14}O$, there was obtained with sodium amide in benzene solution, an amide which Semmler names dihydrocamphoceënic acid amide (b), $C_9H_{17}ON$, and which has the melting point 168°. By saponification, dihydrocamphoceënic acid (b), $C_9H_{16}O_2$ is obtained; b. p. 138 to 139° (12 mm. pressure); $d_{22°}$ 0,9815; n_D 1,45662.

With regard to the constitution of fenchone and camphenilone according to Semmler the two following formulæ come under consideration for the former, which illustrate the similarity between fenchone, as methylcamphenilone, and camphenilone.

I. II. III.



fenchone fenchone camphenilone

Sodium amide appears to be an excellent reagent for such ring-ketones, which next to the CO-group only show alkylised carbon atoms.

Thujone. An analogous communication by A. Kötz[2]), also discussed in this Report, deals with the condensations of cyclopentanone, isothujone, and thujone, with oxalic ester. The production of cyclopentanone-2-oxalic acid ester-1,

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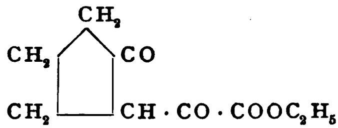
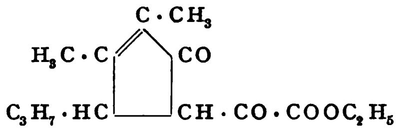
[1]) With regard to Kondakow's view of the correctness of Semmler's fenchone formula, see p. 118.

[2]) Liebig's Annalen **348** (1906), 111; comp. also the present Report p. 148.



results from condensation of pentanone and ethyl oxalate with sodium and absolute alcohol; the ester boils at 14 mm. pressure at 138 to 139°. The corresponding isothujone oxalic ester (dimethyl-1,5-isopropyl-4-cyclopentene-5-one-2-oxalic acid ester-3)



boils at 182 to 184° (11 mm. pressure); its semicarbazone melts at 168 to 169°. Thujone oxalic acid ester (methyl-2-isopropyl-5-bicylo-[0,1,3-]hexanone-3-oxalic ester-4) boils at 168 to 170° (11 mm. pressure), and yields a semicarbazone melting at 156 to 157°. The crystals (m. p. 253,5°) separating off when the ester was boiled with aniline in alcohol, were identified as oxanilide. Attempts to effect a separation of carbonic oxide from cyclopentane-2-oxalic acid ethyl ester-1, and also from thujone oxalic ester, did not succeed, and a conversion of the latter into thujone oxalic acid also failed. The pentacyclic oxalic esters described behave for the rest like the derivatives of cylohexanone, *i. e.,* they are split up by soda liquor into the ketone and oxalic acid. On the other hand, the former are, contrary to the latter, are very stable when heated *in vacuo*, (slight inclination to split off carbonic oxide), but when heated under ordinary or increased pressure, they are split up into carbonic oxide, carbon dioxide, alcohol, and the corresponding ketones, instead of passing over (like the hexacyclic compounds) into the β-keto-carboxylic esters. This difference in the behaviour of cyclic ketone-oxalic esters, when heat is applied, enables us to ascertain whether a CH_2-group, adjacent to the CO-group, is situated in a cyclopentane or in a cyclohexane ring.

Pulegone. In connection with previous researches for the knowledge of addition-processes[1]), D. Vorländer[2]) and his collaborators have also made experiments with pulegone. The action of sodium malonic ester on pulegone[3]) takes place as follows: In the presence of benzene or ether, the anhydride of an alkyl ester acid of pulegone malonic acid is formed, probably as follows:

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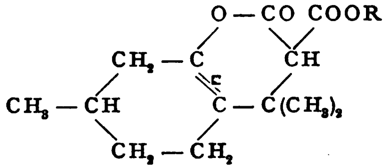
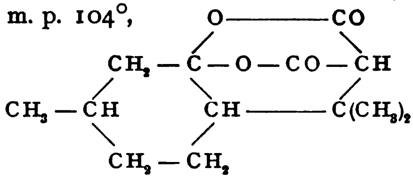
1) Liebig's Annalen **341** (1905), 1.
2) Ibidem **345** (1906), 155.
3) D. Vorländer and Fr. Köthner, ibidem **345** (1906), 158.

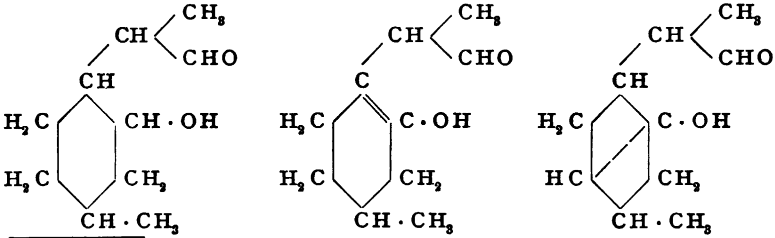


By saponification with alkali liquor, the unstable pulegone malonic acid is obtained, and from the latter the beautifully crystallising keto-dilactone of the m. p. 104°,



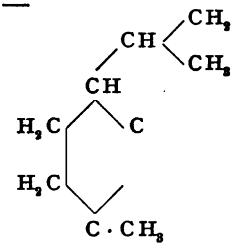
and from this, by the action of alcohol and sulphuric acid, pulegone malonic acid dialkyl ester. The latter is split up by absolute-alcoholic sodium alcoholate, with dissolution of the carbon-linking, into pulegone and sodium malonic ester, so that the dissolving action of the alcoholate is opposed to its condensing action. Like in all dissociations, the medium plays here also the principal part. In the presence of benzene the addition predominates; in alcoholic solution, the rupture. By splitting off carbon dioxide (at 203 to 204°) there is obtained from the dilactone of pulegone malonic acid, pulegone acetic anhydride (m. p. 103°)[1]). The production of a series of derivatives succeeded both with pulegone malonic and with pulegone acetic acids. The keto-dilactone can be very readily obtained in a good yield by treating dry pennyroyal oil with sodium malonic ester. Attempts to produce other characteristic keto-dilactones from ring ketones had negative results with tanacetone, dihydrocarvone, carone, and camphorphorone, but with benzalmenthone it succeeded to some extent.

Diosphenol. According to Kondakow and Bachtschiew[2]), the following formulæ came up to the present under the consideration for the constitution of diosphenol, if on the one hand $C_{10}H_{18}O_2$, or on the other $C_{10}H_{16}O_2$ is accepted as the gross formula: —

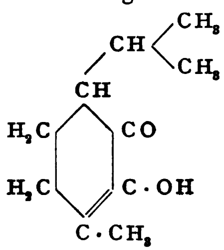


[1]) A. May and W. König, ibidem **345** (1906), 188.
[2]) Comp. Report April **1901**, 91.

By their recent investigations Semmler and McKenzie[1]), have succeeded in accomplishing the degradation as well as the synthesis of diosphenol. They found the melting point of the repeatedly recrystallised diosphenol at 83 to 84°, the boiling point at 109 to 110° (10 mm. pressure). It is inactive, dissolves gradually in lyes, reduces other bodies, is readily oxidised, and imparts in alcoholic solution a pink colour to fuchsin solution decolorated by sulphurous acid. When diosphenol was acetylated, benzoylated, or brought into reaction with carbanil, one oxygen atom always reacted, the other one remained intact. The phenyl urethane of diosphenol melted at 41°. The oxime (m. p. 125°) could not be converted into the nitrile. When heated in a sealed tube with hydrochloric acid to 150 to 180°, thymol is formed quantitatively (b. p. 115° [12 mm. pressure]; $d_{20°}$ 0,9777; n_D 1,5219; phenyl urethane, m. p. 107°), with a small quantity of carvacrol. With semicarbazide and phenylhydrazin, diosphenol gives but a feeble reaction. According to Semmler diosphenol represents a monocyclic saturated keto-alcohol $C_{10}H_{16}O_2$. He draws this conclusion from the oxidation with ozone, whereby α-isopropyl-γ-acetyl-n-butyric acid is formed. This would explain that 9 carbon and 15 hydrogen atoms are linked as follows: —

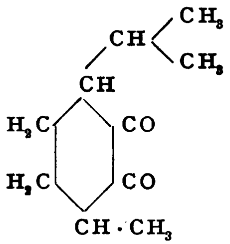


whilst the position of the last carbon (or hydrogen) atom is shown by the reduction into the glycol $C_{10}H_{20}O_2$. This is oxidised into α-isopropyl-α'-methyl-n-adipic acid, which favours the acceptance of a 6-ring with the methyl- and isopropyl-groups in para-position. Semmler consequently accepts for diosphenol, as the first hydrated phenol proved with certainty, the following formula: —

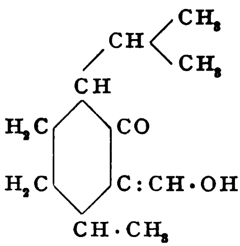


[1]) Berl. Berichte **39** (1906), 1158.

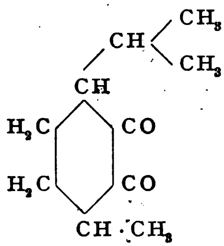
against the tautomeric diketo form:



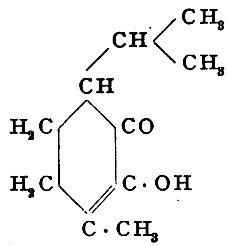
But the production of a diosphenol reacting as a diketone has not yet succeeded. Derivatives of diosphenol which have been produced, are p-menthane-diol-2, 3 (b. p. 135 to 137° at 10 mm. pressure) obtained by reduction of diosphenol with sodium and alcohol, and the dibromo-derivative $C_{10}H_{14}Br_2O_2$. — In synthetising diosphenol, Semmler and McKenzie started from hydroxymethylene-menthone, which was oxidised into the diketone, and in an acid medium was already partly inverted into the enolic form. The inversion is completed in alkaline or acid solution. The reaction-mechanism may be illustrated by the following graphic formulæ: —



hydroxymethylene-menthone
(b. p. 120° [11 mm. pressure]; $d_{20°}$ 0,994; ^{11}D 1,49668)



diketone



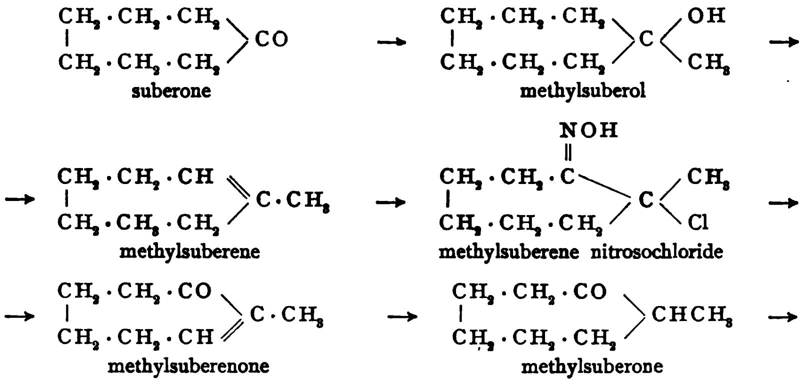
diosphenol

The oxidation of hydroxymethylene-menthone with ozone in aqueous solution gives a still better yield, but a certain amount of care must be observed as the oxidation is easily carried too far. The synthetic buchu camphor was identical in its properties with the natural one.

Suberone. Since v. Baeyer's assumption that tetrahydroeucarvone should be regarded as trimethylsuberone, must be accepted as established by Wallach[1]), the latter[2]) now proposes the following way for producing substituted cyclic heptenones and heptanones, with the

[1]) Liebig's Annalen **339** (1905), 97; Report October **1905**, 113.
[2]) Liebig's Annalen **345** (1906), 139.

help of Grignard's reaction, and by making use of his own well-known method of building up ketones from unsaturated hydrocarbons[1]):



By the action of methylmagnesium iodide on suberone, and by decomposition of the double compound formed with sulphuric acid, methylsuberol is obtained, which by heating with bisulphate in a current of hydrogen passes over easily with loss of water into Δ_1-methylsuberene (Δ_1-methyl-1-cycloheptene), C_8H_{14}; d 0,824; b. p. 137,5 to 138,5°; $n_{D19,5°}$ 1,4581. Wallach indicates for this hydrocarbon the two following possible formulæ: —

I. II.

Now the hydrocarbon (formula II) previously[2]) produced by Wallach from suberene acetic acid, agrees on the whole in its physical properties with the one mentioned above, but from a chemical point of view the two show a totally different behaviour, and for this reason formula I no doubt belongs to methylsuberene. As, in view of the method of production, another isomerisation was not impossible, the correctness of the formula was also tested by an oxydative degradation of the hydrocarbon. The hydrocarbon, as might be expected from formula I, was oxidised to ε-acetylcaproic acid, $CH_3 \cdot CO \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot COOH$, and the degradation of the keto acid to normal pimelic acid with hypobromite was also carried out easily.

The nitrosate and the nitrosochloride of the hydrocarbon were obtained in a good yield, 70 and 65 to 67% respectively; both

[1]) Comp. Reports April **1903**, 92; April **1904**, 124; October **1904**, 128.
[2]) Liebig's Annalen **314** (1900), 158.

can then be readily converted with sodium methylate into methylsuberane methyloxime, which corresponds to the formula

$$\begin{array}{l} CH_2 - CH_2 - C(NOH) \\ | \\ CH_2 - CH_2 \text{———} CH_2 \end{array} \Big\rangle C \Big\langle \begin{array}{l} OCH_3 \\ \\ CH_3 \end{array}$$

As in the reaction the acid radical (NO_3 or Cl) is substituted by OCH_3, it is not a question of a simple oxime. The 7-ring system, therefore, with entirely analogous changes shows a smaller inclination to the formation of an ethylenic linking in the ring than the 6-ring system. If by means of tertiary bases (dimethylaniline) 1 mol. hydrochloric acid is split off from methylsuberene nitrosochloride, the oxime of methyl suberenone is obtained. The ketone regenerated in the usual manner from the semicarbazone (m. p. 162 to 163°) has the following properties: d 0,9695; n_{D21° 1,4867; b. p. 200 to 205°. By reducing methylsuberenone in alcoholic solution with sodium, an alcohol was obtained (though only in a small yield, owing to an abundant formation of pinacone) which was oxidised with chromic acid to methyl-1-cycloheptanone-2 (methylsuberone), which, however, for the present could only be detected in the form of its semicarbazone of the m. p. 129 to 131°.

Several years ago already[1]) Wallach has, as the first synthetic methene hydrocarbon[2]), built up methene suberene (methene cycloheptamethylene) from suberone; it should only be noted that in his recent investigations on the subject[3]), he condensed suberone and bromoacetic ester with magnesium instead of zinc, and with the addition of iodine. A comparison of methene suberene with the linking-isomeric methylsuberene showed, as already stated, a decided analogy of the physical constants; only the totally different chemical behaviour proved the difference in their constitution. Methene suberene, contrary to β-phellandrene, showed no tendency to autoxidation. According to Wallach the pronounced oxidability of β-phellandrene is not due to the ethylene linking adjacent to the methene, for sabinene, which contains one methene group has an equally indifferent behaviour as methene suberene. The glycol:

$$\begin{array}{l} CH_2 \cdot CH_2 \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \cdot CH_2 \end{array} \Big\rangle C(OH)CH_2(OH)$$

produced from it by oxidation with 1 per cent. potassium permanganate solution, melts at 50 to 51°, and when brought in contact with dilute

1) Liebig's Annalen **314** (1900), 147; Report April **1901**, 61.
2) Liebig's Annalen **343** (1905), 28; Report April **1906**, 114.
3) Liebig's Annalen **345** (1906), 146.

acids, passes over immediately, with loss of water, into suberane aldehyde

$$\left.\begin{array}{l}CH_2\,CH_2\,CH_2\\ |\\ CH_2\,CH_2\,CH_2\end{array}\right> CH\cdot CHO$$

which is of particular interest being the first synthetic aldehyde of a 7-ring system. The oxime, from which the aldehyde could be regenerated, distilled over between 110 and 120°, but could not be made to crystallise. The semicarbazone of the aldehyde melted at 153 to 154°. By oxidation with silver oxide this yielded then the silver salt of heptamethylene carboxylic acid. As a by-product of the permanganate oxidation there is formed oxysuberane carboxylic acid (m. p. 78°), which was identified by its difficultly soluble sodium salt. The conversion of methene suberene into the corresponding aldehyde is accomplished in the following phases:

$$\begin{array}{ccccccc}(C_8H_{12}) & & (C_8H_{12}) & & (C_8H_{12}) & & (C_8H_{12})\\ \vee & \rightarrow & \vee & \rightarrow & \vee & \rightarrow & \vee\\ C=CH_2 & & C(OH)CH_2\cdot(OH) & & C=CH\cdot OH & & CH\cdot CHO\\ \text{methene suberene} & & \text{glycol} & & \text{(unstable)} & & \text{suberane aldehyde}\end{array}$$

The nitrosochloride of methene suberene yields on treatment with sodium methylate, with loss of hydrochloric acid, an oxime, which produces by means of sulphuric acid the unsaturated suberene aldehyde,

$$\left.\begin{array}{l}CH_2\cdot CH_2\cdot CH\\ |\\ CH_2\cdot CH_2\cdot CH_2\end{array}\right> C\cdot CHO,$$

which is converted by oxidation into the corresponding acid, suberene carboxylic acid (m. p. 50 to 51°). According to this, the nitrosochlorides or nitrosates of the methene compounds can also be used for the production of unsaturated alicyclic aldehydes, the same as they have already for a long time been employed for producing unsaturated ketones.

Cyclohexanone.[1]) Whilst 1,3-methyl-cyclohexanone was already made accessible 10 years ago by Wallach[2]) by splitting up pulegone, this was with 1,2-and-1,4-methyl cyclohexanones only accomplished by the well-known reduction-method of Sabatier. All three ketones have a similar odour; the boiling points increase (though but slightly) with the distance of the two atom-groups CH_3 and CO. The specific gravity is fairly equal in 1,3- and 1,4-methylhexanone, but is higher in 1,2-methylhexanone. The capacity of auto-condensation varies; with

[1]) Wallach, Liebig's Annalen, **346** (1906), 249.
[2]) Comp. Reports October **1896**, 92; April **1897**, 56; October **1904**, 127.

benzaldehyde 1,2-methylhexanone condenses to a bright-yellow oil (probably a monobenzylidene compound); 1,3-and-1,4-methylhexanone yield deep-yellow dibenzylidene compounds. The boiling point of 1,2-methylhexanone lies at 164 to 165°, a fact which has been confirmed not only by Wallach, but also by Sabatier and W. H. Perkin; d 0,926; n_{D20° 1,4493; oxime, m. p. 43 to 44°. For 1,4-methylhexanone the following constants were observed: b. p. 169 to 171°; d 0,914; n_{D20° 1,44315; its oxime melts at 37 to 39° and boils at 114° (14 mm. pressure). With 2 mol. benzaldehyde the ketone condenses to a dibenzylidene compound of the m. p. 98 to 99°. From a further work by Wallach[1] on the two isoximes of 1,3-methylcyclohexanone it appears that to the *α*-isoxime the formula belongs given further down. It was namely found that this body, when boiled with hydrochloric acid, splits up, with formation of the hydrochloride of an amido acid, which on oxidation with permanganate in alkaline solution yields *β*-methyl adipic acid (m. p. 86°). The following formulæ may represent the progress of the conversion: —

$$\underset{\alpha\text{-isoxime}}{\left.\begin{array}{l} CH_2 \cdot CH(CH_3) \cdot CH_2 \\ | \\ CH_2 \cdot CH_2 \text{———} NH \end{array}\right\rangle CO} \rightarrow \underset{\text{amido acid}}{\begin{array}{l} CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot COOH \\ | \\ CH_2 \cdot CH_2 \cdot NH_2 \end{array}}$$

$$\rightarrow \underset{\beta\text{-methyladipic acid}}{\begin{array}{l} CH_2 \cdot CH(CH_3) \cdot CH_2 \cdot COOH \\ | \\ CH_2 \cdot COOH \end{array}}$$

The *β*-isoxime was split up into the amido acid by boiling with hydrochloric acid, and the hydrochloride of the acid, from which the excess of acid had been removed as much as possible, yielded after treatment with sodium nitrite and oxidation of the hydroxy acid formed with permanganate, in addition to bicarboxylic acids, a keto acid whose semicarbazone melted at 177°, and which is identical with *γ*-acetyl-butyric acid. The reaction is as follows: —

$$\underset{\beta\text{-isoxime}}{\left.\begin{array}{l} CH_2CH(CH_3)CH_2 \\ | \\ CH_2 \text{———} CH_2CO \end{array}\right\rangle NH} \rightarrow \underset{\text{amido acid}}{\begin{array}{l} CH_2CH(CH_3)CH_2NH_2 \\ | \\ CH_2CH_2COOH \end{array}}$$

$$\rightarrow \underset{\text{hydroxy acid}}{\begin{array}{l} CH_2CH(CH_3)CH_2OH \\ | \\ CH_2CH_2COOH \end{array}} \rightarrow \begin{array}{l} CH_2CH(CH_3)COOH \\ | \\ CH_2\,CH_2\,COOH \end{array} \rightarrow \underset{\gamma\text{-acetyl-butyric acid}}{\begin{array}{l} CH_2\,CO\,CH_3 \\ | \\ CH_2\,CH_2\,COOH \end{array}}$$

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[1]) Liebig's Annalen **309** (1899), 2; **312** (1900), 194; **332** (1904), 348.

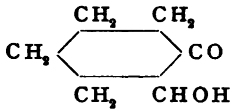
The two isomeric trimethylcyclohexanones, methyl-1-dimethyl-3,3-cyclohexanone-5 (dihydroisophorone)[1]), and methyl-1-dimethyl-3,3-cyclohexanone-6, readily form oximes of the m. p. 84 to 85°, and 108 to 109° respectively, from each of which by treatment with dilute sulphuric acid two isomeric isoximes are obtained. The higher-melting, more difficultly soluble α-modifications of the isoximes melt at 111 to 112° and 113 to 116° respectively, the β-modifications at at 82 to 84° and 106 to 108° respectively.

In agreement with previous observations made with l-menthone[2]), Wallach also succeeded in producing from 1,3-methylcyclohexanone, by reduction of the β-oxime, β-methylcyclohexylamine. The use of the ammonium formiate method[3]) for this reaction resulted, in addition to the primary, also in much of the secondary base. But it could now be proved that this consists of a mixture of physically isomeric bases, of which two were isolated by fractionated precipitation with formic acid. α-Cyclodimethylhexylamine forms a hydrate which, with loss of water, melts at 46 to 48°; the β-forms hows no tendency to crystallise with water, but remains liquid. From the α-base, the following derivatives were produced: 1. The benzoyl compound $(C_7H_{13})_2N \cdot COC_6H_5$, m. p. 141°; $[\alpha]_D - 34{,}646°$ (in ethereal solution). 2. The nitroso compound $(C_7H_{13})_2 : N \cdot NO$, m. p. 83 to 84°; $[\alpha]_D - 34°$ (in ethereal solution). 3. The phenyl carbamide, m. p. 174 to 176°. The β-base gave the following derivatives; 1. The benzoyl compound, m. p. 151°; $[\alpha]_D - 11{,}877°$ (in alcoholic solution). 2. The nitroso compound, which could not be obtained in a well-crystallised form, m. p. between 62 and 70°, rotation lower than in the α-compound. 3. The phenyl carbamide, m. p. 137 to 138°, has a more feeble rotation than the derivative of the α-base. The hydrochloride of the α-base (m. p. 285°) is separated off more quickly than that of the β-base (m. p. 211°); nitrate and nitrite dissolve with difficulty and are fairly stable.

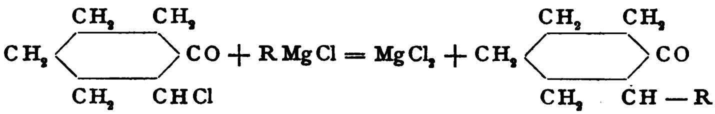
By the action of chlorine on cyclohexanone there is obtained, according to E. Bouveault aud E. Chereau[4]), α-chlorocyclohexanone. But in addition to this, condensation-products are formed, owing to the action of the hydrochloric acid formed. In order to prevent the formation of free hydrochloric acid, the chlorination is carried out in the presence of calcium carbonate in water, and the cyclohexanol is chlorinated instead of the cyclohexanone. Chlorocyclohexanone boils at 82 to 83° (10 mm. pressure) and melts at 23°. The chlorine

[1]) Comp. Report April **1903**, 93.
[2]) Liebig's Annalen **300** (1898), 278; Report October **1898**, 49.
[3]) Comp. Report April **1906**, 134.
[4]) Compt. rend. **142** (1906), 1086.

atom in the molecule is fairly mobile. Hot concentrated potash solution hydroxylises the body to α-hydroxycyclohexanone

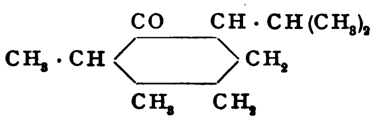


which the authors designate as "adipoine". This body sublimes at 100° (ordinary pressure) and melts at 113°, its semicarbazone at 165°. Its constitution is shown, analogous to that of chlorocyclohexanone, on oxidation with permanganate by the formation of adipic acid. Grignard's salts condense with chlorocyclohexanone according to the equation: —



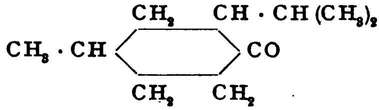
In an analogous manner are produced: α-methylcyclohexanone, b. p. 60° (10 mm. pressure); semicarbazone, m. p. 195°; α-ethylcyclohexanone, b. p. 65° (10 mm. pressure); semicarbazone m. p. 157°; α-isopropylcyclohexanone, b. p. 80° (10 mm. pressure).

In connection with the synthesis[1] of menthone from methyl-3-cyclohexanone already discussed by us, Kötz publishes jointly with A. Michels[2] a synthesis of m-menthanone-2 and m-menthanone-4 from methyl-1-cyclohexanone-2 and methyl-1-cyclohexanone-4. By the action of oxalic ester on these cyclohexanones, the authors obtained the corresponding ketone esters. Methyl-1-cyclohexanone-2-oxalic acid ethyl ester-3 passed over, by splitting off carbonic oxide, into methyl-1-cyclohexanone-2-carboxylic ethyl ester-3 boiling at 115° (12 mm. pressure), whose semicarbazone melts at 140°. Methyl-1-cyclohexanone-4-oxalic acid ethyl ester-3 yielded methyl-1-cyclohexanone-4-carboxylic ethyl ester-3, b. p. 110° (10 mm. pressure); semicarbazone, m. p. 134°. By saponifying the bodies converted into their isopropyl esters by means of sodium ethylate and isopropyl iodide, and by splitting off carbon dioxide, the authors finally arrived at methyl-1-isopropyl-3-cyclohexanone-2 (m-menthanone-2)



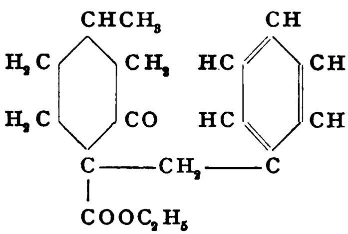
[1]) Liebig's Annalen **342** (1905), 306; Report April **1906**, 126.
[2]) Liebig's Annalen **348** (1906), 91.

(b. p. 82° [10 mm. pressure]; d_{15° 0,9128), and methyl-1-isopropyl-3-cyclohexanone-4 (m-menthanone-4)

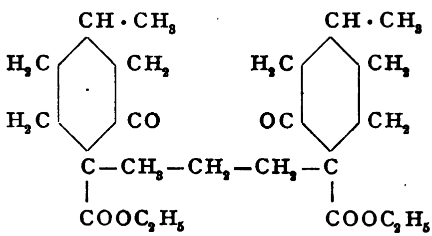


(b. p. 195°; d_{15° 0,8914), whose oxime melts at 105°.

In conjunction with G. Kayser, A. Kötz[1]) has also worked on the production of systems with two nuclei, in which one benzene nucleus occurs combined with one hydrated benzene nucleus, or two hydrated benzene nuclei combined indirectly. By the action of benzyl chloride on methyl-1-cyclohexanone-3-carboxylic ester-4, with the use of sodium ethylate, there was formed methyl-1-benzyl-4-cyclohexanone-3-carboxylic ester, which was obtained by distillation at 194° (12 mm. pressure); its semicarbazone melts at 169°. By boiling the ester with methyl alcoholic potash liquor, methyl-1-benzyl-4-cyclohexanone-3 is formed, which is driven off by water vapour under pressure. Its boiling point lies at 173° (13 mm. pressure), at 166° (10 mm. pressure), its semicarbazone melts at 172° and its oxime at 139°. If to a mixture of the original product and sodium ethylate, p-nitrobenzylchloride is added, there is obtained methyl-1-p-nitrobenzyl-4-cyclohexanone-3-carboxylic ester-4, melting at 90,5°. For the production of dimethyl-1,1′-trimethylene-4-dicyclohexanone-3,3′-dicarboxylic ester-4,4′, trimethylene bromide is introduced under otherwise analogous conditions into the reaction-mixture. The ester boils at 257 to 263° (18 mm. pressure) and can be converted with methyl alcoholic potash into the corresponding ketone, whose semicarbazone melts at 107°. The oil regenerated from the latter with sulphuric acid melts at 204°. The formulæ of the bodies described are as follows: —



methyl-1-benzyl-4-cyclohexanone-3-carboxylic ester-4



dimethyl-1, 1′-trimethylene-4-dicyclohexanone-3, 3′-dicarboxylic ester-4,4′

1) Ibidem **348** (1906), 97.

The constitution of the remaining derivatives can be traced from these formulæ. Attempts to produce the corresponding esters with bromacetophenone, methylene iodide, and ethylene bromide, did not lead to the expected results.

Cyclopentanone. See under thujone, the present Report, p. 138.

Acids.

Cinnamic acid. We learn from a work by E. Erlenmeyer jun. and C. Barkow[1]) on stereo-isomeric cinnamic acids that the authors have proved the existance of a new cinnamic acid. We had placed at the disposal of Prof. Erlenmeyer two preparations, the one from the oil of *Alpinia malaccensis*[2]), and the other from so-called Honduras balsam[3]). Whereas the former preparation consisted of small leaflets, the latter crystallised in fine small curved needles, which showed a totally different habit than all other preparations observed up to the present. From the crystallographic measurement made by A. Fock, it was found that it was a question of a new cinnamic acid. Further examinations showed that the one acid (α-cinnamic acid) could be converted into the other (β-cinnamic acid), and *vice versâ*. Interesting is the behaviour of synthetic cinnamic acid and storax cinnamic acid in 75 per cent. alcohol, by means of which the two above-named investigators hope to bring about a separation of the constituents of which synthetic cinnamic acid is formed. To the six cinnamic acids differing crystallographically as well as otherwise, viz., isocinnamic acid of Erlenmeyer sen., allocinnamic acid, isocinnamic acid of Liebermann, triclinic cinnamic acid, α-cinnamic acid from storax, and β-cinnamic acid from storax, must still be added the isocinnamic acid from the more readily soluble brucine salt, which in the crystalline form differs but slightly from Liebermann's, and the synthetic acid which both in the crystal-formation and in the salt-formation with brucine shows distinct differences from all the others.

Phenols and phenol ethers.

Asarone. By reducing asarone with sodium and alcohol, Székí[4]) obtained an oil which boiled at 185 to 188° (40 mm. pressure), and was identified by the analysis as dihydroasarone $(CH_3O)_3C_6H_2 \cdot CH_2 \cdot CH_2 \cdot CH_3$. The author's opinion that dihydroasarone was not yet

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[1]) Berl. Berichte **39** (1906), 1570.
[2]) Comp. Gildemeister and Hoffmann, The Volatile Oils, p. 313.
[3]) Comp. Tschirch, Schweiz. Wochenschr. f. Chem. u. Pharmacie **43** (1905), 238; Report April **1906**, 96.
[4]) Berl. Berichte **39** (1906), 2419.

known is not correct, for Thoms[1]) has already examined the products of the action of nitric acid on dihydroasarone, and Ciamician and Silber[2]) have also 16 years ago worked on dihydroasarone. — Széki also produced asarone dibromide, $(CH_3O)_3 C_6 H_2 \cdot CHBr \cdot CHBr \cdot CH_3$, m. p. 83°, which had already been obtained by B. Rizza and A. Butlerow[3]), but had not yet been examined further, and he observed that asarone is readily oxidised by iodine and mercuric oxide to α-2, 4, 5-trimethoxyphenylpropionic aldehyde, which at normal pressure boils at 275° without decomposition. The fact that isoeugenol and isosafrol can be polymerised by treatment with acetyl chloride or mineral acids, induced Széki[4]) to extend this reaction also to isoapiol, isoeugenol methyl ether, and asarone. The bodies obtained, diisoapiol, diisoeugenol methyl ether, and diisoasarone, melt at 97°, 106° and 100° respectively.

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1) Ibidem **36** (1903), 854.
2) Ibidem **23** (1890), 2283.
3) Ibidem **17** (1884), 1159.
4) Ibidem **39** (1906), 2422.

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Systematic Experiments

on the

Antiseptic Action of Essential Oils and their Constituents

by

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There are a large number of microbes capable of hydrolysing the molecule of free sulphur in the presence of albumins. As the sulphuretted hydrogen thus formed can readily be detected by means of lead acetate paper, the occurrence of this hydrolysis can conveniently be followed up. On the other hand, it is naturally also easy to determine with the aid of this method, whether an antiseptic agent added impairs the formation of sulphuretted hydrogen, or (as the case may be) arrests it altogether. As not everybody has pure cultures of bacteria at disposal, it is interesting to know that according to experiments[1]) made at our Institute by Hermann Brüning, the so-called normal milk bacteria, as present in all milk of marketable quality, bring about this formation of sulphuretted hydrogen with great certainty, if finely powdered sulphur is added to the milk and the latter placed for 24 hours in the incubator. Of pure cultures of bacteria which can be used for the same purpose, Brüning has found, for example, *Bacterium coli* very useful. At the suggestion of Prof. Kobert, he has made comparative experiments on the antiseptic action of numerous essential oils and their constituents[2]), according to this method. As milk, although obtained from the same source, and of the same age, is not always exactly uniform with regard to its content of bacteria, it appeared desirable to take up the experiments once more and extend them in some directions, before the publication or abstraction of Brüning's results in these Reports. These experiments I have carried out, and embodied them also in the table lower down.

The milk-experiments were made in the following manner. Quantities of 10 cc. each of raw cow's milk were placed in test tubes and mixed with finely powdered sulphur, as much as would lie on the point of a knife, in the form of sulphur præcipitatum. Next there were added to the milk by means of the same pipette in increasing quantities, namely 1, 2, 4, 6, 8, 12, 16, 20, 24, 32 drops and finally 1 cc., the essential oils (or their constituents) of which the action was to be tested. It goes without saying that one cc. does not with every oil contain the same number of drops. In some test tubes only

[1]) Brüning, Über das Verhalten des Schwefels zu Milch (und Milchpräparaten) sowie zur Schleimhaut des Magendarmkanales [On the behaviour of sulphur towards milk (and milk preparations) and also towards the mucous membrane of the gastro-intestinal canal]. (Zeitschr. f. exp. Path. u. Therap.).

[2]) Brüning, Ätherische Öle und Bakterienwirkung in roher Kuhmilch [Essential oils and bacterial action in raw cow's milk] (Centralbl. f. inn. Mediz. 27 [1906], No. 14).

milk and sulphur were placed, for purposes of control. After the tubes had been well shaken, strips of filtering paper impregnated with a solution of sugar of lead, were pressed in the openings by means of plugs of cotton wool. These plugs at the same time prevented the entrance of bacteria from the air to the milk. It was, namely, desirable that the milk should contain as nearly as possible the same bacterial flora. For this reason the milk was always obtained from the same place, kept in the same manner without special precautions, and worked up at the same time after obtaining it. The tubes were left standing for 24 hours in a water-bath of 38 to 40° C. On the following day an examination was made, whether or not the added substance had prevented the blackening of the lead paper, *i. e.*, whether or not it had acted as an antiseptic.

Next, the number of drops required to prevent the blackening were read off. From the number of drops belonging to one cc., the volume proportionate to the milk was then calculated, and the concentration and the intensity of the antiseptic action thereby determined. According to their intensity, the antiseptics were placed in five groups, as shown by the following table:

The development of H_2S is prevented by a dilution of:	The antiseptic power was designated as:
below 1 in 10	very feeble
1 in 10 to 1 in 25	feeble
1 in 25 to 1 in 50	medium strong
1 in 50 to 1 in 100	strong
above 1 in 100	very strong

This systematic division has also formed the basis of the table of substances examined.

The reader will perhaps be astonished that Brüning and I characterise the antiseptic power as very strong if it is above 1 in 100, whilst in many experiments mentioned in literature, a very strong action is only spoken of at 1 in 10000. This apparent contradiction can thus be explained, that in all series of experiments in which it is desired to obtain the best results for an antiseptic, a medium is selected which impairs the antiseptic power as little as possible, and which promotes the vitality of the microbes to the least possible extent. But in our experiments purposely the opposite conditions were selected, for on the one hand, we used the most favourable possible nutritive medium for the milk bacteria, viz., raw milk, — and on the other hand, the total quantity of the essential oil added, which in being dissolved in the milk passed over in the fat globules of the latter, was abstracted from the aqueous solution, and was thus prevented from acting in that aqueous solution which contained the bacteria. Just for this

reason we consider such experiments as those which we made, as particularly important, for they are a safeguard against overestimating the value of our remedies. These methods of examination, which are as unfavourable for the antiseptics as it is possible to make them, have hitherto generally been purposely avoided for most remedies, although in practice they are imperatively required.

The expression "entire essential oils" in the following table means the mixtures of all the substances contained in the oils. Of the most usual constituents, those examined were alcohols, aldehydes, ketones, phenols and phenol ethers, terpenes, esters, and various representatives of other classes of bodies.

A. Entire essential oils.

below 1 in 10	1 in 10 to 1 in 25	1 in 25 to 1 in 50	1 in 50 to 1 in 100	above 1 in 100
Amber oil	Angelica oil	Basil oil	Bay oil	Bitter almond oil, natural and artificial[4]
Anise oil	Citronella oil[2]	Eucalyptus oil	Cajeput oil	Cassia oil
Bergamot oil	Geranium oil	Linaloe oil	Caraway oil	Cherry laurel oil
Calamus oil	Jaborandi leaf oil	Niobe oil	Coriander oil[1]	Cinnamon oil
Cardamom oil	Lavender oil	Orange blossom oil	Dill oil[1]	Clove oil
Cedarwood oil	Patchouli oil	Palmarosa oil	Double Caraway oil	Mustard oil, natural and artificial
Celery oil	Peppermint oil	Europ. Pennyroyal oil	Jasmine oil	Spike oil
Copaiba balsam	Peru balsam	Rosemary oil	Pine needle oil[1]	
Cubeb oil	Pinus montana oil	Sage oil	Spearmint oil	
Cumin oil	Rue oil		Spoonwort oil, natural[1]	
Cypress oil	Sandalwood oil		Spoonwort oil, artificial	
Erigeron oil	Tansy oil		Turpentine oil, ozonised[3]	
Estragon oil	Thuja oil		Wormseed oil	
Fennel oil	Wild Thyme oil		Ylang Ylang oil	
Ginger oil	Wormwood oil			
Juniper berry oil				
Lemon oil				
Lemongrass oil				
Lovage oil				
Matico oil				
Nutmeg oil				
Orange oil				
Parsley oil				
Savin oil				
Turpentine oil, free from oxygen[3]				
Valerian oil				
Wintergreen oil, artificial and natural				

[1]) According to Brüning above 1 in 100.
[2]) According to Brüning 1 in 50 to 1 in 100.
[3]) According to Brüning 1 in 25 to 1 in 50.
[4]) According to Brüning below 1 in 10.

B. Constituents of essential oils.

Substances	below 1 in 10	1 in 10 to 1 in 25	1 in 25 to 1 in 50	1 in 50 to 1 in 100	above 1 in 100
I. **Alcohols**	Ethyl alcohol Santalol	Citronellol Geraniol		Furfuric alcohol Linalool [2]) Terpineol [2])	Benzylic alcohol
II. **Aldehydes**	Citral Heliotropin	Citronellal			Anisic aldehyde Benzaldehyde (art. oil of bitter almonds [1])) Cinnamic aldehyde
III. **Ketones**	Muskone Thujone		Carvone Methyl heptenone Pulegone	Fenchone Menthone	
IV. **Phenols and phenol ethers**	Anethol Apiol Isomyristicin Isosafrol Methyl chavicol Thymol	Safrol	Myristicin	Eugenol	Isoeugenol
V. **Terpenes**	Camphene Dill oil terpenes Phellandrene Rosemary oil terpenes	Bay oil terpenes Citronella oil terpenes Pinene	Terpinene [1])	Limonene	
VI. **Esters and organic salts**	Amyl ester of salicylic acid Methyl ester of salicylic acid (art. Wintergreen oil) Bornyl acetate Bornyl valerianate Linalyl acetate		Benzyl acetate Methyl ester of benzoic acid		
VII. **Various**	Coumarin Tinctura moschi		Cymene Eucalyptol (cineol)		body $C_{10}H_{16}O_2$ from wormseed oil

[1]) According to **Brüning** below 1 in 10.
[2]) According to **Brüning** above 1 in 100.